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Unsymmetrical organolead compounds

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NOTE TO USERS

UNSYMMETRICAL ORGANOLEAD COMPOUNDS

by

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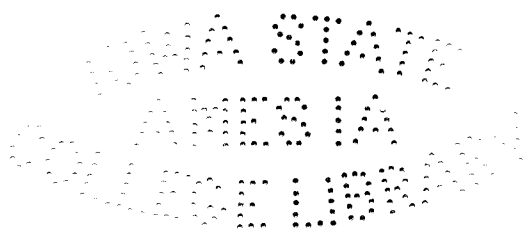

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENT	2
INTRODUCTION	7
HISTORICAL	11
Preparation of R_nMM' Compounds	11
R_3SiM'	11
R_3GeM'	13
R_3SnM'	19
R_3PbM'	26
R_2BiM'	29
R_3BM'	30
Generalizations	30
Preferential Cleavage of Organometallic Compounds by Sodium	31
Properties of R_nMM' Compounds	38
R_3SiM'	38
R_3GeM'	39
R_3SnM'	41
R_3PbM'	46
EXPERIMENTAL	49
Cleavage of Symmetrical Organolead Compounds by Metals	49
Conditions influencing cleavage of tetraphenyllead	49
Solvents	50
Temperature	51
Amount of ethyl bromide for derivatization	52
Different metals	52
Presence of sodamide	54
Removal of sodamide	55
Filtration	55

Page

Addition of ammonium bromide 55
Addition of excess ammonium bromide. 56

Time 56
Excess sodium 57
Optimum conditions 63

Conditions influencing cleavage of tetraethyllead 63

Solvents 63
Temperature 65
Amount of n-butyl bromide for derivatization 66

One equivalent 66
One and one-half equivalents 67
Two equivalents 68
Five equivalents 68

Different metals 69
Removal of sodamide 70

Filtration 70
Addition of ammonium bromide 70

Excess metal 71
Optimum conditions 73

Cleavage of Organolead Compounds in Inert Solvents. 74

With the binary system (Mg + MgI_2) 74
With sodium amalgam 75
With sodium 75

Reaction of Organolead-sodium with Organic Halides. 77

Triphenyllead-sodium 77

Ethylene dibromide 77
p-Chlorotoluene 79
p-Bromotoluene 80
p-Iodotoluene 80
Methyl p-bromobenzoate 81
p-Iodonitrobenzene 82
2,4-Dinitrochlorobenzene 83

Triethyllead-sodium 83

Page

Methyl bromide 83
Benzyl chloride 84
t-Butyl bromide 86
Iodobenzene 88
Bromobenzene 90
Allyl chloride 90
s-Butyl bromide 91

Trimethyllead-sodium 92

Bromobenzene 92

Preferential Cleavage of Organolead Compounds . . . 93

Triethyl-n-butyllead 94

Cleavage by different metals 94

Calcium 95
Lithium 95
Sodium 96

Identification of diethyl-n-butyl-methyllead 96

Triethylallyllead 97

Cleavage by sodium 97

Triethylbenzyllead 98

Cleavage by sodium 98

Triethyl-s-butyllead 100

Cleavage by sodium 100
Identification of diethyl-s-butyl-methyllead 101

Triethylmethyllead 102

Cleavage by sodium 102

Triethylphenyllead 103

Cleavage by lithium 103
Identification of diethylmethyl-phenyllead 104

Page

Trimethylphenyllead 105

Cleavage by sodium 105

Triphenyl-p-dimethylaminophenyllead 106

Cleavage by sodium 106

DISCUSSION 109

Preparation of Organolead-sodium Compounds 109

Reaction of Organolead-sodium Compounds with Organic Halides 119

Preferential Cleavage of Organolead Compounds . . . 127

Suggested Mechanism of the Cleavage of Organolead Compounds by Metals 135

SUMMARY 139

APPENDIX 140

INTRODUCTION

Since organolead compounds have been shown to be effective in arresting cancer (1), much research has been done in an effort to increase the effectiveness of these compounds in combating this dreadful disease. Recent studies show that water soluble derivatives are the most efficacious of the organolead compounds (2); therefore, the preparation of water soluble organolead drugs is a problem of prime importance.

In general, a molecule may be made more soluble in water by the introduction of polar groups, such as -COOH, $-SO_3H$, $-NH_2$, $-NR_2$, etc. Although organic chemists know what groups should be attached to increase the water solubility of a compound, they experience difficulty in finding a general method of introducing such groups into the organolead molecule. A comparison of the methods of preparing symmetrical organolead compounds with those of preparing the unsymmetrical derivatives indicated that the latter methods were more favorable for the introduction of polar groups. For this reason, attention was

(1) (a) Krause, Ber., 62, 135 (1929); (b) Robinson, Doctoral Dissertation, Iowa State College (1929).
(2) Schmidt, Med. u. Chem. Abhandl. med.-chem. Forschungsstätten I. G. Farbenind., 3, 418 (1936) [C.A., 31, 5866 (1939)].

turned to the study of unsymmetrical organolead compounds.

Unsymmetrical organolead compounds are ones in which at least two different organic groups are attached to lead by carbon-lead bonds. On the basis of their structures, these compounds may be divided into two different classes. Members of the first class have only organic groups attached to the lead atom, that is, $R_3R'Pb$, $R_2R'_2Pb$, $R_2R'R''Pb$, and $RR'R''R'''Pb$ (3); but members of the second class, mixed unsymmetrical organolead compounds, have inorganic groups as well as organic groups attached directly to the lead atom, that is, $R_2R'PbX$, $RR'R''PbX$, and $RR'PbX_2$ (3).

The present investigation was undertaken to test the applicability of the recently discovered coupling reaction of organolead-sodium compounds (4) with alkyl halides [equation I]

$$R_3PbM' + R'X \longrightarrow R_3PbR' + M'X \qquad [I]$$

as a method of introducing polar groups. Orientation experiments were planned to test the limitations of this coupling reaction as influenced by the following factors: the type of R group on the organolead-sodium compounds, the kind of reactive metal (M'), the negativity of the R' group in the organic halide (R'X), the reactivity of the halogen in the organic

(3) R indicates an organic group, and the superscript shows that one organic group is different from the other. X is used to represent an inorganic group, such as a halogen, hydroxide, nitrate, etc.

(4) The suggested nomenclature for this type of compound is in the Appendix of this thesis (p. 141).

halide, and the polar groups which may be present in the RX compound.

In the course of this work, it was found that the carbon-lead linkage of organolead compounds could be cleaved by sodium in liquid ammonia to yield solutions of organolead-sodium compounds, a reaction which made these reagents much more easily available. The cleavage reaction was run under many different sets of conditions to determine how the reaction should be carried out to obtain the maximum yields of organo-lead-sodium compounds. Later, the reaction of sodium with organolead compounds was extended to a study of the preferential cleavage of groups from unsymmetrical organolead molecules. Former studies in preferential cleavages of organometallic compounds have been criteria for arranging groups in order of decreasing ease of cleavage. This series of groups, Kharasch's series, is valuable as a guide for chemists when predicting the extent and course of many different types of reactions. When the groups are arranged in order of decreasing ease of cleavage, they fall in the same general order although the cleaving agent is varied. Cleaving agents that have been used are acids, halogens and salts. It was thought that metals, a quite different type of cleaving agent, might give an altogether different series when the organic groups were arranged in order of decreasing ease of cleavage. These results should give more valuable information on the

applicability of Kharasch's series.

This work, then, was undertaken to study, first, the preparation of organolead-sodium compounds by the cleavage of organolead molecules with sodium; second, the reaction of organolead-sodium compounds with organic halides; and, third, the preferential cleavage of unsymmetrical organolead compounds.

HISTORICAL

Although little information concerning R_3PbM' compounds has been published, similar members of the R_nMM'(5) type have been studied in some detail. The number of metals that form this type of compound is small, inasmuch as definite evidence for the existence of R_nMM' compounds has been reported only where M represents Si, Ge, Sn, Pb, Bi and perhaps B.

Knowledge of the chemistry of known members should serve as a valuable guide in understanding the properties of a new member of the same general type. Our first task, then, should be a review of the literature concerned with R_nMM' compounds.

Preparation of R_nMM' Compounds

R_3SiM'

Organosilicon halides were more available than most organosilicon compounds; therefore, it was desirable to attempt to use the halides as starting materials for the preparation of organosilicon-sodium compounds. However, R_3SiNa compounds could not be obtained when organosilicon halides in liquid

(5) The significance of each symbol is: R, an organic group; n, a small integer; M, one of the following metals Si, Ge, Sn, Pb, Bi, or B; and M', a metal that is soluble in liquid ammonia.

ammonia were treated with sodium, since these halides underwent ammonolysis too readily (6).

Triethylsilicon bromide reacted readily with liquid ammonia, but did not react with ethylamine. This latter fact indicated that triethylsilicon-lithium may be produced in ethylamine from the reaction of triethylsilicon bromide and lithium. The reaction did not proceed in the predicted manner (7), however, since the product was triethyl(ethylamino)silicon. The equation proposed by Kraus and Nelson to explain the results was

$$2(C_2H_5)_3SiBr + 2Li + 2C_2H_5NH_2 \longrightarrow 2(C_2H_5)_3SiNHC_2H_5 + 2LiBr + H_2$$

Since a hydrogen attached to silicon is rather labile, it seemed reasonable to expect triethylsilicon hydride to undergo a reaction with lithium in ethylamine and yield triethylsilicon-lithium; but instead, the hydride reacted with the solvent, ethylamine, under the catalytic influence of lithium, as shown in the following equation (7):

$$(C_2H_5)_3SiH + C_2H_5NH_2 \longrightarrow (C_2H_5)_3SiNHC_2H_5 + H_2$$

Another discouraging result, obtained by Kraus and Nelson, was the failure of hexaethyldisilicon and lithium to react in ethylamine. They expected triethylsilicon-lithium to be

(6) (a) Kraus and Kahler, J. Am. Chem. Soc., 55, 3537 (1933); (b) Kraus and Sherman, ibid., 55, 4694 (1933); (c) Kraus and Rosen, ibid., 47, 2739 (1935).
(7) Kraus and Nelson, ibid., 56, 195 (1934).

produced. In a similar attempt, it was found that hexaethyldisilicon was not cleaved by a solution of sodium in liquid ammonia. Solutions of metals in ammonia or amines are the most powerful reducing agents known. These results emphasize the tenacity of the silicon-silicon bond, since these attempted reactions show that this bond cannot be broken by the strongest of reducing agents. Because the germanium-germanium bond is cleaved by these strong reducing agents, as mentioned in the following section, Kraus and Nelson reasoned that the germanium to silicon bond would be weaker than the silicon-silicon bond. Their prediction was found to be valid, when they showed that (triethylsilicyl)triphenylgermanium was cleaved by lithium to yield triethylsilicon-lithium.

$$(C_2H_5)_3SiGe(C_6H_5)_3 + 2Li \longrightarrow (C_2H_5)_3SiLi + (C_6H_5)_3GeLi$$

This is the only reported preparation of R_3SiM' compounds, and since these reaction products have never been separated, organosilicon-metal compounds have never been prepared in the pure state.

R_3GeM'

Organogermanium-sodium compounds, in contrast to the corresponding organosilicon derivatives, can be prepared free of other organometallic impurities, as demonstrated by Kraus

and Foster (8). Triphenylgermanium-sodium, the first germanium compound of this type to be reported, was made by the reaction of sodium with hexaphenyldigermanium in liquid ammonia (8).

$$[(C_6H_5)_3Ge]_2 + 2Na \longrightarrow 2(C_6H_5)_3GeNa$$

Although the reaction was slow, the yield of product was practically quantitative.

Solutions of impure triphenylgermanium-sodium in liquid ammonia were obtained by substituting sodium for either the hydrogen of triphenylgermanium hydride [equation II] or for the phenyl group of tetraphenylgermanium [equation III].

$$2(C_6H_5)_3GeH + 2Na \longrightarrow 2(C_6H_5)_3GeNa + H_2 \qquad [II]$$

$$(C_6H_5)_4Ge + 2Na + NH_3 \longrightarrow (C_6H_5)_3GeNa + NaNH_2 + C_6H_6 \quad [III]$$

The supposition was made by Kraus and Foster that when the concentration of sodium was too high, this reactive metal also substituted for a phenyl group of the primary product, triphenylgermanium-sodium, to yield some of the red diphenylgermanium-disodium.

$$(C_6H_5)_3GeNa + 2Na + NH_3 \longrightarrow (C_6H_5)_2GeNa_2 + NaNH_2 + C_6H_6 \quad [IV]$$

The supposition of the formation of diphenylgermanium-disodium was supported by two observations, neither of which was conclusive. The first observation was the replacement of the blue by a red color during the reaction of sodium with

(8) Kraus and Foster, ibid., 49, 457 (1927).

triphenylgermanium-sodium in liquid ammonia. Since the red color was not characteristic of the starting materials, it must be due to a new product. Because red was the typical color of liquid ammonia solutions of organotin-disodium compounds (9), this same color in the case of germanium compounds was assumed to be due to a compound of similar structure, diphenylgermanium-disodium. Later, diphenylgermanium-disodium was shown to be red (10). The second observation, which supported the supposed substitution, was the formation of a liquid organogermanium compound when the red solution, prepared by the reaction of triphenylgermanium hydride with excess of sodium, was treated with ammonium bromide. The product was a mixture of a solid, presumably triphenylgermanium hydride, and a liquid which could not be induced to crystallize at -33°. Without purifying, derivatizing or analyzing this liquid, Kraus and Foster assumed it was diphenylgermanium dihydride, and they also assumed that the presence of the dihydride was a result of treating the supposed diphenylgermanium-disodium with ammonium bromide. Later, Kraus and Brown (10) showed that diphenylgermanium dihydride could not be isolated as a product of the reaction of diphenylgermanium-disodium and ammonium bromide. This observation challenged the assumption of Kraus and Foster that the liquid

(9) See p. 25 of this thesis.
(10) Kraus and Brown, J. Am. Chem. Soc., 52, 4031 (1930).

they obtained was diphenylgermanium dihydride; therefore, the contention that the reaction represented by equation [IV] took place is largely speculative and is supported only by the development of a red color.

Triphenylgermanium-sodium was also formed by the reaction of triphenylgermanium oxide with sodium (11).

$$[(C_6H_5)_3Ge]_2O + 2Na \longrightarrow (C_6H_5)_3GeNa + (C_6H_5)_3GeONa$$

The reaction continued rather rapidly until two equivalents of sodium were used, but although a considerable excess of sodium was added, the $(C_6H_5)_3GeONa$ could not be converted to triphenylgermanium-sodium. The reaction of triphenylgermanium oxide with sodium was not an important method for the preparation of triphenylgermanium-sodium, because an impure product was obtained, and not all of the germanium was converted to the desired product.

The preparation of trialkylgermanium-sodium compounds proved to be a more difficult task than the preparation of the corresponding aryl compounds. The difficulty, for the most part, was the result of two properties of alkylgermanium compounds. First, when three of the groups on the germanium were alkyl rather than aryl groups, the fourth group was more difficult to cleave from germanium. Second, trialkylgermanium-sodium compounds, being more reactive than the corresponding

(11) Kraus and Wooster, ibid., 52, 372 (1930).

aryl derivatives, were destroyed by ammonolysis. Hexaethyldigermanium did not react appreciably with sodium in liquid ammonia, but when ether was added, the germanium compound did react slowly to produce triethylgermanium-sodium (12). Hexaethyldigermanium reacted more readily in ethylamine with the more electropositive metal, lithium. Unfortunately, the product, triethylgermanium-lithium, underwent solvolysis slowly in ethylamine and more rapidly in liquid ammonia to yield triethylgermanium hydride. Since the potassium derivative was more resistant to solvolysis, practically a quantitative yield of triethylgermanium-potassium was obtained by the reaction of hexaethyldigermanium and potassium in ethylamine. Potassium, then, is the metal of choice for the preparation of aliphatic R_3GeM' compounds.

Since triphenylgermanium hydride reacted only slowly and incompletely with sodium, one would predict that triethylgermanium hydride either would not react or would react with difficulty under the same conditions. Kraus and Flood (12) found that triethylgermanium hydride did not react with sodium in liquid ammonia.

Inorganic groups were removed from certain mixed organogermanium compounds by reactive metals, but the inorganic groups were not always replaced by the metal. Part of the oxygen of

(12) Kraus and Flood, ibid., 54, 1635 (1932).

triethylgermanium oxide was removed by lithium in ethylamine, apparently with the formation of triethylgermanium-lithium; but solvolysis took place during evaporation of the solvent (12). On the other hand, all of the halogen of triethylgermanium bromide was replaced when a liquid ammonia solution of the bromide was treated with sodium. However, triethylgermanium-sodium was not found as a product (12). The vigorous evolution of hydrogen during the reaction with sodium indicated that ammonolysis of the triethylgermanium bromide took place in liquid ammonia when sodium was present, but ammonolysis did not take place under the same conditions when sodium was absent. The sodium probably acted either as a catalyst or as a reagent to shift an equilibrium. By using ethylamine as the solvent and lithium as the metal, Kraus and Flood (12) were able to prepare triethylgermanium-lithium from triethylgermanium bromide.

Since $R_2GeM'_2$ compounds are very similar to R_3GeM' compounds, information concerning members of the former class may well be included in this discussion. Diphenylgermanium-disodium was produced by the reaction of tetraphenyldigermanium with a liquid ammonia solution of sodium (10). The color changes indicated that the reaction proceeded through an intermediate stage (yellow) before forming the diphenylgermanium-disodium (red).

$$[(C_6H_5)_2Ge]_2 + 2Na \longrightarrow Na(C_6H_5)_2GeGe(C_6H_5)_2Na \xrightarrow{+2Na} 2(C_6H_5)_2GeNa_2$$

More distantly related compounds are sodium derivatives of germanium hydrides ($NaGeH_3$) and certain alloys (Na_4Ge_x). Reviews of earlier work on these and similar derivatives of other metals are given in papers by Kraus (13) and Fernelius and Bowman (14).

R_3SnM'

Since organotin halides do not undergo ammonolysis in liquid ammonia, the reaction between trimethyltin chloride and sodium in this solvent gave a quantitative yield of trimethyltin-sodium (15).

$$(CH_3)_3SnCl + 2Na \longrightarrow NaCl + (CH_3)_3SnNa$$

Trimethyltin bromide (16), triethyltin bromide (17), and triphenyltin chloride (17) all reacted in this manner with sodium in liquid ammonia. This method was also used to prepare the first unsymmetrical R_nRMM' compound, diethylmethyltin-sodium, by the treatment of a liquid ammonia solution of diethylmethyltin bromide with sodium (18).

Sodium reacted with trimethyltin hydride in liquid ammonia in the expected manner, since hydrogen was evolved and trimethyltin-sodium was formed (15). Sodamide also reacted to some

(13) Kraus, Chem. Rev., 26, 95 (1940).
(14) Fernelius and Bowman, ibid., 26, 3 (1940).
(15) Kraus and Greer, J. Am. Chem. Soc., 44, 2629 (1922).
(16) Kraus and Sessions, ibid., 47, 2361 (1925).
(17) Kraus and Bullard, ibid., 48, 2131 (1926).
(18) Bullard and Vingee, ibid., 51, 892 (1929).

extent with trimethyltin hydride in liquid ammonia to produce a mixture of trimethyltin-sodium and trimethyltin amide (19).

Although $(C_6H_5)_3GeONa$ did not react with sodium in liquid ammonia (11), a very similar tin compound, triethyltin hydroxide, did react with this metal under the same conditions to yield triethyltin-sodium (20). Likewise, trimethyltin amide was converted to trimethyltin-sodium by the addition of sodium (19). These results are in accord with the generalization that inorganic groups are more readily removed from the R_3MX compounds if the M has a higher atomic number.

The most important method of preparing rather pure solutions of triorganotin-sodium compounds is the treatment of hexaorganoditin compounds with sodium in liquid ammonia. This method was used to prepare both trimethyltin-sodium (15) and triethyltin-sodium (20).

None of the R_nMM' compound previously discussed in this report were prepared by cleavage of organic groups from the R_4M compounds, but this type of reaction can be carried out in the case of tin compounds. Kraus and Sessions (16) found that trimethyltin-sodium was formed from the reaction of tetramethyltin with sodium in liquid ammonia. The reactions proposed to explain these products were

(19) Kraus and Neal, ibid., 52, 695 (1930).
(20) Harada, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 35, 290 (1939) [C.A., 33, 5357 (1939)].

$$(CH_3)_4Sn + 2Na \longrightarrow (CH_3)_3SnNa + CH_3Na$$

$$CH_3Na + NH_3 \longrightarrow CH_4 + NaNH_2$$

Later, Kraus (13) mentioned that it was by no means certain that methylsodium was actually formed as an intermediate compound, but no evidence was presented to oppose this suggestion. Other organotin-sodium compounds that have been prepared by this method are triethyltin-sodium (20) and triphenyltin-sodium (21).

Little work has been done on the reactions of unsymmetrical organotin compounds with liquid ammonia solutions of metals. This work was important, not as a method of preparing organotin-sodium compounds, but as a method of studying preferential cleavage of groups from organotin molecules. Sodium reacted with unsymmetrical organotin compounds to replace one organic group with a sodium atom. The reaction of sodium with methylenebis(trimethyltin) probably followed the course shown in the following equations which were proposed by Kraus and Neal (19).

$$(CH_3)_3SnCH_2Sn(CH_3)_3 + 2Na \longrightarrow (CH_3)_3SnNa + NaCH_2Sn(CH_3)_3$$

$$NaCH_2Sn(CH_3)_3 + NH_3 \longrightarrow NaNH_2 + (CH_3)_4Sn \qquad [V]$$

$$(CH_3)_4Sn + 2Na + NH_3 \longrightarrow (CH_3)_3SnNa + NaNH_2 + CH_4$$

It is equally possible that the reaction proceeded as follows:

(21) Chambers and Scherer, J. Am. Chem. Soc., 48, 1054 (1926).

$$(CH_3)_3SnCH_2Sn(CH_3)_3 + 2Na \longrightarrow (CH_3)_3SnCH_2Sn(CH_3)_2Na + CH_3Na$$

$$CH_3Na + NH_3 \longrightarrow CH_4 + NaNH_2 \qquad [VI]$$

$$(CH_3)_3SnCH_2Sn(CH_3)_2Na + 2Na \longrightarrow (CH_3)_3SnNa + NaCH_2Sn(CH_3)_2Na$$

$$NaCH_2Sn(CH_3)_2Na + NH_3 \longrightarrow (CH_3)_3SnNa + NaNH_2$$

A similar experiment, which has not been reported, would establish with certainty whether mechanism [V] or [VI] is the correct one. This suggested experiment involves the treatment of methylenebis(trimethyltin) with only two equivalents of sodium, then, the derivatization of the resulting organotin-sodium compounds by the addition of methyl iodide. Tetramethyltin would be the product if the cleavage proceeds according to mechanism [V], but methylenebis(trimethyltin) would be the product if the cleavage proceeds according to mechanism [VI].

Another interesting cleavage (22) of an unsymmetrical organotin compound resulted from the reaction of sodium with a liquid ammonia solution of a compound that was presumably vinylenebis(trimethyltin). The supposed vinylenebis(trimethyltin) was prepared by the reaction of trimethyltin-sodium with chloroform. This reaction was thought to proceed according to the following equations:

$$3(CH_3)_3SnNa + CHCl_3 \longrightarrow [(CH_3)_3Sn]_3CH + 3NaCl$$

$$2[(CH_3)_3Sn]_3CH \longrightarrow 2[(CH_3)_3Sn]_2 + (CH_3)_3SnCH{=}CHSn(CH_3)_3$$

In confirmation of the mechanism suggested, two moles of

(22) Kraus and Neal, ibid., 52, 4426 (1930).

trimethyltin were obtained for one mole of the supposed vinylenebis(trimethyltin). The tin analysis and the molecular weight checked the theoretical values for vinylenebis(trimethyltin). However, more evidence is needed to substantiate fully the structure of this compound; especially since the per cents of carbon and hydrogen found did not check with the calculated values. Because the compound was difficult to burn evenly, the experimental values for the per cents of carbon and hydrogen were thought to be in error; therefore, these values were discarded. The structure of this compound should not be considered to be proved until the compound has also been either derivatized or synthesized by a reliable method.

As mentioned before, this supposed vinylenebis(trimethyltin) was cleaved with sodium in liquid ammonia; and upon evaporation of the solvent, the mixture of organotin-sodium compounds was more stable and had more of a bright yellow color than was characteristic of trimethyltin-sodium alone. These observations were used as indications that another organotin-sodium compound, presumably dimethylvinyltin-sodium, was present.

$$(CH_3)_3SnCH{=}CHSn(CH_3)_3 + 2Na \longrightarrow (CH_3)_3SnNa + NaCH{=}CHSn(CH_3)_3$$

$$NaCH{=}CHSn(CH_3)_3 + NH_3 \longrightarrow CH_2{=}CHSn(CH_3)_3 + NaNH_2$$

$$CH_2{=}CHSn(CH_3)_3 + 2Na + NH_3 \longrightarrow CH_2{=}CHSn(CH_3)_2Na + CH_4 + NaNH_2$$

This mixture of yellow compounds was treated with methyl iodide and produced a liquid which was presumably a mixture of tetramethyltin and trimethylvinyltin. A fractional vaporization of

the liquid was carried out, and the molecular weight of each fraction was determined. The molecular weights of the fractions increased steadily from 181.1 to 190.9. The lowest value corresponds closely to the molecular weight of tetramethyltin (178.8) and the highest value corresponds closely to that of trimethylvinyltin (190.8). Kraus and Neal, in this report, mentioned that this evidence for the existence of trimethylvinyltin is still inconclusive.

This cleavage was of interest, if the equations are correct, because this was the preparation of the first R_3MM' compound containing an unsaturated aliphatic group [CH_2=$CHSn(CH_3)_2Na$]. It was of interest also to observe that the [-CH=$CHSn(CH_3)_3$] group was cleaved before the methyl group.

Triphenyltin-sodium, contaminated with triphenylmethylsodium, was formed by the cleavage of triphenyltriphenylmethyltin (23).

$$(C_6H_5)_3SnC(C_6H_5)_3 + 2Na \longrightarrow (C_6H_5)_3SnNa + (C_6H_5)_3CNa$$

This reaction is of little importance for the preparation of the organotin-sodium compound because of the simultaneous formation of triphenylmethylsodium. It should be noted, however, that the triphenylmethyl group rather than the phenyl group was cleaved from the unsymmetrical organotin compound. The significance of this observation will be mentioned in connection with preferential cleavage of groups from organometallic

(23) Bailie, Doctoral Dissertation, Iowa State College (1939).

compounds.

Compounds having the formula NaR_2SnSnR_2Na are slightly different structurally than those having the formula R_3SnM, but since the two types are closely related chemically, compounds of the former type may properly be mentioned in this discussion. The first one of the tetraorganoditin-disodium compounds to be prepared was made by Kraus and Greer (24) when they added sodium to polymerized dimethyltin in liquid ammonia:

$$2(CH_3)_2Sn + 2Na \longrightarrow Na(CH_3)_2SnSn(CH_3)_2Na$$

Evidence for the formation of this product was, first, that a characteristic color (yellow) developed and, second, that when methyl iodide was added, hexamethylditin was produced. Harada (20) prepared the corresponding ethyl compound by adding sodium to diethyltin.

Another closely related type of compound that should be included is the disodium derivative, R_2SnNa_2. Kraus and Greer (24) gave the first report of this type of compound also. The method they applied to prepare dimethyltin-disodium was the addition of sodium to tetramethylditin-disodium.

$$Na(CH_3)_2SnSn(CH_3)_2Na + 2Na \longrightarrow 2(CH_3)_2SnNa_2$$

This same reaction has been applied to the preparation of other diorganotin-disodium compounds. Chambers and

(24) Kraus and Greer, J. Am. Chem. Soc., 47, 2568 (1925).

Scherer (21) applied it to the preparation of a diaryltin-disodium compound, diphenyltin-disodium. They found that it was not necessary to carry out the addition of sodium in a stepwise fashion, or to isolate the intermediate compounds: that is, diphenyltin dichloride reacted with four equivalents of sodium to yield diphenyltin-disodium. Later, Harada (20) showed that diethyltin-disodium could also be prepared by the addition of sodium to diethyltin dibromide.

R_3PbM'

Kraus and Kahler (6a), reporting on the conductivity of R_3MNa compounds of the Group IV metals, made the statement, "Excepting the derivatives of tin and lead, the salts are stable in the pure state." This statement indicated that they tried to prepare an organolead-sodium compound, but they mentioned nothing else concerning this type of lead compound and gave no experimental details.

Gilman and Bailie (25) presented the first definite evidence of the existence of an R_3PbNa compound. They prepared a solution of the supposed triphenyllead-sodium by adding sodium to a liquid ammonia solution of hexaphenyldilead. The supposed organolead-sodium was then derivatized by the addition of benzyl

(25) Gilman and Bailie, ibid., 61, 731 (1939).

chloride, and triphenylbenzyllead was isolated. The production of this unsymmetrical organolead compound proved that triphenyllead-sodium was present before the addition of benzyl chloride. Gilman and Bailie also prepared the R_3PbNa compounds in which the R represented the p-tolyl, o-anisyl, cyclohexyl, or p-ethoxyphenyl group.

Soon afterward, Foster and coworkers (26) confirmed the preparation of triphenyllead-sodium and added that hexaphenyldilead also reacted with tetrasodium nonaplumbide to give triphenyllead-sodium. While the reaction of hexaphenyldilead with sodium gives a quantitative yield of triphenyllead-sodium, good yields of this product, although slightly less pure, are obtained also from the reaction of triphenyllead halides with the same metal.

Sodium is not the only metal that reacts with hexaphenyldilead to yield an R_3MM' compound. Leeper (27) prepared the lithium, potassium, rubidium, calcium, strontium, and barium derivatives of triphenyllead by the reaction of a liquid ammonia solution of the metal with hexaphenyldilead. He also prepared the calcium and lithium derivatives of triethyllead by the reaction of triethyllead chloride and the metal in liquid ammonia.

(26) Foster, Dix and Gruntfest, ibid., 61, 1685 (1939).
(27) Leeper, unpublished studies.

Bailie (23) showed that triphenyllead-sodium was produced when triphenyltriphenylmethyllead was treated with sodium in liquid ammonia. Addition of benzyl chloride to the resulting solution gave a mixture of triphenylbenzyllead and 1,1,1,2-tetraphenylethane. The formation of these two products proved that triphenyllead-sodium and triphenylmethylsodium were produced during the initial reaction; therefore, the triphenylmethyl group rather than the phenyl group was cleaved from triphenyltriphenylmethyllead.

Some $R_2PbM'_2$ compounds were prepared by the reaction of diphenyllead dihalides with several metals: lithium, sodium, potassium, calcium, strontium, and barium (28). The highest yields of diphenyllead-dimetal compounds were obtained by the reaction of diphenyllead dibromide or dichloride with either lithium or sodium. Again, liquid ammonia was used as the reaction medium. The reagents had to be added in a certain order; that is, the diphenyllead dihalide had to be added to a solution of the metal in liquid ammonia. The reactions of diphenyllead dihalides appear to be quite complex; because after adding ethyl bromide to derivatize the expected diphenyllead-disodium, Apperson isolated tetraethyllead, triethylphenyllead, and triphenylethyllead as well as the expected diphenyldiethyllead.

The formation of this mixture of products may be

(28) Apperson, Doctoral Dissertation, Iowa State College (1940).

partially explained in two ways. The first explanation is that the diphenyllead dihalide reacted with sodium in a very complex manner to produce a mixture of $PbNa_4$, $C_6H_5PbNa_3$, $(C_6H_5)_2PbNa_2$, and $(C_6H_5)_3PbNa$; then each of these compounds reacted in the normal way with ethyl bromide to yield $Pb(C_2H_5)_4$, $C_6H_5Pb(C_2H_5)_3$, $(C_6H_5)_2Pb(C_2H_5)_2$, and $(C_6H_5)_3PbC_2H_5$, respectively. The second explanation is that the diphenyllead dihalide reacted with sodium in the expected manner to produce only diphenyllead-disodium, but the latter compound reacted in a complex manner with ethyl bromide to yield the mixture of organolead compounds. We cannot say, at present, which is the correct explanation.

R_2BiM'

Organometal-sodium compounds of only one Group V metal, bismuth, have been proved to exist. Diphenylbismuth-metal compounds were prepared by the reaction of a liquid ammonia solution of a diphenylbismuth halide with sodium, potassium, lithium, calcium, and barium (29). Also, the organic group may be varied, for diorganobismuth-sodium compounds were prepared in which the organic groups were either phenyl, p-tolyl, or p-chlorophenyl groups.

(29) Gilman and Yablunky, J. Am. Chem. Soc., 63, 212 (1941).

R_3BM'

These organoboron-sodium compounds differ from other R_nMM' compounds in two respects: first, the apparent valence of the boron is higher than the normal valence of boron; and second, these compounds are prepared in ether, not in liquid ammonia or ethylamine. Further investigations will undoubtedly show more differences between organoboron-sodium compounds and the other R_nMM' compounds mentioned in this thesis. The monosodium (30) and disodium (31) derivatives of tri-α-naphthylboron, as well as the monosodium derivative of triphenylboron (30), were prepared by the reaction of the triarylboron compounds with sodium amalgam in ether, but little further work has been done on these compounds.

Generalizations

One may now draw some generalizations concerning the methods of preparation of R_nMM' compounds.

(a) The reaction of R_nMMR_n with M', as a rule, gives the most pure R_nMM', but the starting material, particularly a hexaalkyldilead compound, is the least readily available.

(b) The reaction of R_nMX with M' is the one usually

(30) Bent and Dorfman, ibid., 57, 1259 (1935).
(31) Bent and Dorfman, ibid., 54, 2132 (1932).

applied, because the yields are good and the starting material is more easily obtained than in method (a).

(c) R_nMH reacts with M′ to produce R_nMM', but the starting material is not readily available and has never been prepared in the case of the lead compounds.

(d) The reaction of R_4M with M′ to yield R_3MM' is not applicable for those compounds in which M has a low atomic number (Si), but is more applicable for cases in which M has a higher atomic number (Sn). This increasing applicability indicates that this reaction may become the most important method of preparing R_3PbM', if the yields are satisfactory, since R_4Pb types are the most readily available of the organolead compounds.

Preferential Cleavage of Organometallic Compounds by Sodium

In the preceding section, it should be noticed that almost every method of preparing R_nMM' compounds involved the cleavage of a group from an organometallic compound and the replacement of that group with the metal used for cleavage. Although these reactions were not run as attempts to study the preferential cleavage of groups from organometallic compounds, the results may be used as an aid in formulating the generalizations on preferential cleavage which are given in the latter part of this section. The first part of this section is concerned with

a review of other reactions involving the preferential cleavage of groups where no attempt was made to prepare R_nMM' compounds.

With silicon compounds, Kraus and Nelson (7) found that sodium in liquid ammonia did not react with triethylphenylsilicon; however, lithium in ethylamine did react with both triethylbenzylsilicon and triethylphenylsilicon. Since no gas was evolved and no aromatic hydrocarbons were detected, it is certain that cleavage of the silicon-carbon bonds did not take place. It was suggested that the aromatic groups were reduced by the metals.

The halogen was removed before the ethyl group when triethylgermanium halides were treated with one equivalent of lithium in ethylamine (12). This was the method used to prepare hexaethyldigermanium.

The preferential removal of halogens from both dimethyltin dibromide (24) and diphenyltin dichloride (21) was used as the best method of preparing dimethyltin and diphenyltin.

Also, in the case of the lead compounds, the addition of one equivalent of sodium to a liquid ammonia solution of trimethyllead iodide (32), triethyllead bromide (32), triphenyllead iodide (23), or tri-m-tolyllead bromide (23) caused the removal of the halogen; but the organic groups remained

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

attached to the lead atom.

The halogens were removed before the organic groups from organometallic compounds of the Group III metals, but the reactions were not simple. For example, when diphenylthallium bromide was treated with sodium in liquid ammonia, triphenylthallium, and metallic thallium were obtained (33). The presence of these products indicated that the bromine was removed first, and the resulting diphenylthallium underwent disproportionation. Also, when dimethylgallium chloride reacted with sodium in liquid ammonia, the chlorine was removed, but the resulting dimethylgallium did not undergo disproportionation (34). Although the halogen-gallium bond was broken rather readily, the carbon-gallium bond was cleaved with difficulty. For example, Kraus and Toonder found that the methyl groups were not cleaved from trimethylgallium by sodium in liquid ammonia or by lithium in ethylamine.

Kraus and Kurtz (35) mentioned that the chlorine was undoubtedly removed first when ethylmercuric chloride was treated with sodium in liquid ammonia. Also, they inferred that the carbon-mercury bond may have been cleaved next by the sodium. If the carbon-mercury bond had not been cleaved, the

(33) Gilman and Jones, J. Am. Chem. Soc., 62, 2357 (1940).
(34) Kraus and Toonder, ibid., 55, 3547 (1933).
(35) Kraus and Kurtz, ibid., 47, 43 (1925).

ethylmercury would have undergone disproportionation to yield diethylmercury and mercury (36), but diethylmercury was not one of the products. Therefore, Kraus and Kurtz were probably correct in their inference that the carbon-mercury bond was broken by sodium.

A few attempts were made to cleave organometallic compounds of the Group V elements with metals in liquid ammonia. Triphenylantimony reacted with sodium in this solvent to produce a red color (37). This color may have been due to diphenylantimony-sodium; however, the identity of the product has not been proved. The hydrogen of methylarsenic dihydride was replaced by potassium, but the methyl group remained attached to the arsenic atom (38).

When triphenylchromium iodide was treated with sodium in liquid ammonia, the halogen, rather than the phenyl group, was removed and triphenylchromium was produced (39).

Sodium in liquid ammonia was incapable of removing either the iodine or the methyl group from trimethylplatinum iodide (40).

In liquid ammonia or in ethylamine, the cleavage of

(36) Gilman, "Organic Chemistry", John Wiley and Sons, New York (1938) Vol. I, p. 481.
(37) Woods, unpublished studies.
(38) Johnson and Pechukas, J. Am. Chem. Soc., 59, 2068 (1937).
(39) Hein and Markert, Ber., 61, 2255 (1928).
(40) Lichtenwalter, Doctoral Dissertation, Iowa State College (1938).

organometallic compounds stops, in general, after one group is removed, but in inert solvents the cleavage stops only after all of the groups are removed. There are no reports which allow decisions to be made as to which groups are removed most easily in inert solvents. However, it is of interest to notice that tetraphenyllead was not cleaved by sodium in benzene, but tetraethyllead was slowly cleaved by this metal in several different solvents. The tetraphenyllead was refluxed for twenty-four hours with sodium sand, but no evidence of phenylsodium was obtained (41). Gilman and Young (42) found that tetraethyllead in ether was cleaved by sodium or sodium-potassium alloy to produce ethylsodium. Dibenzofuran was also present, for they were studying the metalation of dibenzofuran by ethylsodium. In cyclohexane also (43), tetraethyllead reacted with sodium to produce ethylsodium which in turn was used to cleave l-menthyl ethyl ether or d-neomenthyl ethyl ether. Likewise, Schlenk and Holtz (44) were successful in preparing ethylsodium by the reaction of tetraethyllead and sodium in gasoline.

Several generalizations may be stated concerning the

(41) F. Moore, unpublished studies.
(42) Gilman and Young, J. Am. Chem. Soc., 57, 1121 (1935).
(43) Hückel and Bretschneider, J. prakt. Chem., 151, 61 (1938).
(44) Schlenk and Holtz, Ber., 50, 262 (1917).

preferential cleavage of groups from organometallic compounds by reactive metals in liquid ammonia or in ethylamine.

(a) The easiest bond to cleave is a metal-metal bond of $R_nM\text{-}MR_n$ compounds.

(b) The next easiest bond to cleave is a metal-halogen or a metal-hydrogen bond.

(c) Organometallic compounds of the Group IV metals arranged in increasing ease of cleavage by metals are R_4Si, R_4Ge, R_4Sn.

(d) The triphenylmethyl group was cleaved before the phenyl group from both triphenyltriphenylmethyltin and the corresponding lead compound.

(e) The $[-CH_2Sn(CH_3)_3]$ group was reported as being cleaved before the methyl group from $(CH_3)_3SnCH_2Sn(CH_3)_3$. This conclusion was drawn by Kraus and Neal (19) without sufficient evidence. A mechanism based on the cleavage of a methyl group first would explain their observations just as well, as discussed earlier in this thesis.

(f) The $[-CH{=}CHSn(CH_3)_3]$ group was reported as being cleaved before the methyl group from $(CH_3)_3SnCH{=}CHSn(CH_3)_3$. This conclusion (22) was drawn without sufficient proof of the structure of the starting material or of the product, as mentioned earlier in this thesis. However, one may expect vinylenebis(trimethyltin) to cleave as reported if one

considers the structure $(CH_3)_3SnCH=CHSn(CH_3)_3$ as a vinylog of $(CH_3)_3SnSn(CH_3)_3$.

(g) The phenyl group was reported as being cleaved from triphenyltin-sodium more easily than the methyl group was cleaved from trimethyltin-sodium. When Chambers and Scherer (21) drew this conclusion, they did so after apparently misreading the experimental conditions reported in some earlier work by Kraus and Sessions. The latter authors (14) cleaved tetramethyltin with only two equivalents of sodium and found that no dimethyltin-disodium was formed; that is, the second methyl group was not removed. Later, Chambers and Scherer cleaved tetraphenyltin with more than two equivalents (the exact amount was not given) of sodium and found that diphenyltin-disodium was produced; that is, the second phenyl group was removed. Chambers and Scherer compared these two experiments on the basis that more than two equivalents of sodium were used in both cases, but this was not true. In the same report, these authors pointed out that if an excess of sodium was not used in cleaving tetraphenyltin, no diphenyltin-disodium was formed; that is, the second phenyl group was not removed. This was the experiment that was run under conditions similar to those used with tetramethyltin, and the second group was not cleaved in either case. Therefore, one cannot say that the phenyl group was cleaved from triphenyltin-sodium more easily than the methyl group was cleaved from trimethyltin-sodium.

Properties of R_nMM' Compounds

One phase of this research, as mentioned earlier, was to study the reaction between R'X and R_3PbNa compounds. The plan eventually was to have polar groups present in the R'X compound in order to introduce such groups into an organolead molecule and thus produce an organolead compound of greater water solubility. It is advisable, first, to review all of the literature concerned with the reactions of R_nMM' compounds; so this review is presented below. All of these reactions were carried out either in liquid ammonia or in ethylamine.

R_3SiM'

Triethylsilicon-lithium (7) is the only reported silicon compound of this type. Since it was prepared by the reaction of (triethylsilicyl)triphenylgermanium with lithium and the products were not separated, all of the reactions given below are reactions of triethylsilicon-lithium in the presence of triphenylgermanium-lithium.

Triethylsilicon-lithium reacted with ammonium bromide to yield triethylsilicon hydride (7).

$$(C_2H_5)_3SiLi + NH_4Br \longrightarrow (C_2H_5)_3SiH + LiBr + NH_3$$

Ethyl bromide reacted with triethylsilicon-lithium to yield the expected tetraethylsilicon (7).

$$(C_2H_5)_3SiLi + C_2H_5Br \longrightarrow (C_2H_5)_4Si + LiBr$$

R_3GeM'

Since triethylsilicon-lithium was stable in both liquid ammonia and ethylamine, it seems peculiar that triethylgermanium-lithium would undergo solvolysis in these media, but Kraus and Flood (12) reported that solvolysis did take place slowly in ethylamine and completely in liquid ammonia. On the other hand, neither triethylgermanium-potassium (12) nor triphenylgermanium-sodium (6a) underwent solvolysis in liquid ammonia.

Reactions of organogermanium-metal compounds must be carried out in the absence of air because triphenylgermanium-sodium was destroyed by oxygen, as shown in the following equation (8).

$$2(C_6H_5)_3GeNa + O_2 \longrightarrow 2(C_6H_5)_3GeONa$$

When working with organogermanium compounds, one must avoid the presence of moisture because water was found to react readily with triphenylgermanium-sodium to yield triphenylgermanium hydride. Likewise, ammonium bromide reacted with triphenylgermanium-sodium and triethylgermanium-lithium to produce triphenylgermanium hydride and triethylgermanium hydride, respectively (12).

The coupling reaction between organogermanium-sodium

compounds and organic or organometallic halides, in liquid ammonia, may be applied to many different types of halides. For example, triphenylgermanium-sodium coupled in the expected manner with bromobenzene (8); methyl iodide (45); ethyl bromide (45), n-propyl, n-butyl, and n-amyl bromides (6b); benzyl chloride (6b); triphenylgermanium fluoride (8); triethylgermanium bromide (6b); trimethyltin bromide (8); and diphenylgermanium dichloride (6a). The dihalide, methylene dichloride, reacted with triphenylgermanium-sodium to yield the expected methylenebis(triphenylgermanium) (45), but more highly halogenated methanes, chloroform and carbon tetrachloride, reacted to produce unexpected products (45). For example, chloroform reacted with triphenylgermanium-sodium to yield a mixture of methylenebis(triphenylgermanium), triphenylgermanium amide, and triphenylmethylgermanium. Also, carbon tetrachloride reacted with triphenylgermanium-sodium, but triphenylgermanium amide was the only product isolated.

The closely related diphenylgermanium-disodium reacted with ammonium bromide, but no diphenylgermanium dihydride could be isolated (10). The complex mixture of products was not completely purified.

(45) Kraus and Nutting, J. Am. Chem. Soc., 54, 1622 (1932).

R_3SnM'

Halides which undergo ammonolysis in liquid ammonia, and thus produce ammonium halides, cannot be used in the presence of organotin-sodium compounds; because ammonium halides rapidly destroy organotin-sodium compounds. For example, both triphenyltin-sodium (21) and trimethyltin-sodium (15) reacted with ammonium bromide to give the corresponding organotin hydrides.

Air will also destroy organotin-sodium compounds. This prediction was based on the observation that oxygen reacted with triphenyltin-sodium, and after hydrolysis of the product, triphenyltin hydroxide was obtained (21).

In general, trimethyltin-sodium coupled well with aliphatic monohalides to give the expected trimethylalkyltin. The halides tried were ethyl bromide (18), benzyl chloride (17), methyl iodide (46), triphenylmethyl chloride (16), and sodium chloroacetate (21).

The products of the reactions between aliphatic polyhalides and organotin-sodium compounds are less predictable. Ethylene dichloride reacted with trimethyltin-sodium to give ethylene and hexamethylditin (16). Methylene dichloride when treated with either triphenyltin-sodium (47) or trimethyltin-sodium (19)

(46) Bullard and Robinson, ibid., 49, 1366 (1929).
(47) Kraus and Eatough, ibid., 55, 5014 (1933).

gave the corresponding $(R_3Sn)_2CH_2$ compound in good yields. Chloroform reacted with triphenyltin-sodium to give mostly the normal product, $[(C_6H_5)_3Sn]_3CH$, and a small amount of hexaphenylditin (47). However, chloroform reacted with trimethyltin-sodium to give a large amount of hexamethylditin and an appreciable amount of a compound which has been assigned the structure $(CH_3)_3SnCH=CHSn(CH_3)_3$ (22). Carbon tetrachloride reacted with triphenyltin-sodium (47), trimethyltin-sodium (22), and triethyltin-sodium (22) to yield the corresponding hexaorganoditin compounds; but the fate of the carbon could not be determined. In an attempt to prove the structure of vinylenebis(trimethyltin), 1,2-dichloroethylene was treated with trimethyltin-sodium, but only hexamethylditin was found as a product (22).

Chambers and Scherer (21) reported that aryl halides did not react with triphenyltin-sodium unless the halogen had been activated by the presence of a negative group ortho or para to the halogen. Their conclusion was based on the observation that p- or m-chloroaniline or sodium o-chlorophenoxide did not couple with triphenyltin-sodium, but both sodium p-bromobenzoate and p-chloronitrobenzene did couple with this organotin-sodium compound. It was mentioned, however, that the products from the last two reactions were unstable and underwent decomposition; consequently, they could not be

properly identified. Aryl halides show more promise of reacting with trialkyltin-sodium compounds than with the triaryltin-sodium compounds. The coupling reaction took place between p-dichlorobenzene and trimethyltin-sodium to yield p-phenylenebis(trimethyltin) (16). The coupling reaction took place to a lesser extent between bromobenzene and trimethyltin-sodium, since only a small amount of trimethylphenyltin was formed. The other products were trimethyltin hydroxide and considerable $[(CH_3)_3Sn]_3N$ and benzene (46).

Since organotin-sodium compounds reacted with bromobenzene, sodium o-chlorophenoxide and the chloroanilines to produce benzene (46), phenol (21), and aniline (21), respectively, it may be that a metal-halogen interconversion took place with subsequent ammonolysis as shown in the following equations.

$$R_3SnNa + C_6H_5Br \longrightarrow C_6H_5Na + R_3SnBr$$

$$C_6H_5Na + NH_3 \longrightarrow C_6H_6 + NaNH_2$$

$$R_3SnNa + R_3SnBr \longrightarrow (R_3Sn)_2 + NaBr$$

Some organometallic halides react with organotin-sodium compounds to couple the organometallic compounds.

$$R_3MX + (CH_3)_3SnNa \longrightarrow R_3MSn(CH_3)_3 + NaX$$

Trimethyltin-sodium reacted in this manner with trimethyltin halides (16), triethyltin bromide (17), and triphenyltin bromide (17). Also, trimethyltin bromide reacted in this way with both triethyltin-sodium and triphenyltin-sodium (17).

This type of reaction was used in attempts to produce compounds which have a tin-lead linkage, as in the reaction of trimethyltin-sodium with trimethyllead chloride, but apparently the product [$(CH_3)_3Sn\text{-}Pb(CH_3)_3$] was unstable (16). The same general method was applied in an attempt to produce a tin-mercury bond by the reaction of triphenyltin-sodium with phenylmercuric iodide, but only hexaphenylditin, phenylmercuric amide, and mercury were found as products (21).

Tetraethylditin-disodium reacted with ethyl bromide to give hexaethylditin (20), and likewise, tetramethylditin-disodium reacted with methyl iodide to give hexamethylditin (24). These reactions were used to prove the structure of the tetraalkylditin-disodium compounds.

An interesting product [$(CH_3)_3Sn(CH_3)_2SnSn(CH_3)_2Sn(CH_3)_3$] was formed by the reaction of tetramethylditin-disodium with trimethyltin bromide. This product was interesting because it contained three successive tin-tin bonds (48).

Sodium reacted with tetraethylditin-disodium and with tetramethylditin-disodium to yield diethyltin-disodium (20) and dimethyltin-disodium (24), respectively.

Diphenyltin-disodium was destroyed by the presence of ammonium bromide and produced the unstable diphenyltin dihydride (21).

Methyl iodide reacted with both dimethyltin-disodium and diphenyltin-disodium to produce tetramethyltin (24) and

dimethyldiphenyltin (46) respectively. In a similar manner, diethyltin-disodium reacted with ethyl bromide to yield tetraethyltin (20). However, an aromatic halide, bromobenzene, when allowed to react with dimethyltin-disodium did not produce dimethyldiphenyltin (46). In contrast to this result, bromobenzene did react with trimethyltin-sodium to give a small amount of trimethylphenyltin; therefore, it may be said that trimethyltin-sodium is more reactive than dimethyltin-disodium.

There is only one report (24) of a reaction of an organic polyhalide with a diorganotin-disodium compound. This report mentioned that dimethyltin-disodium reacted with methylene dichloride, but the reaction was quite complex. The main product was assigned the formula $[(CH_3)_2SnCH_2]_x$.

As would be expected, dimethyltin-disodium reacted with dimethyltin dibromide to produce polymerized forms of dimethyltin (24). The same type of reaction took place between diethyltin-disodium and diethyltin dibromide (20). However, when the ratio of the number of moles of dimethyltin-disodium to dimethyltin dibromide was two to one, a compound of the structure $[Na(CH_3)_2Sn(CH_3)_2SnSn(CH_3)_2Na]$ was formed. This complex compound reacted in the normal way with ethyl bromide and with trimethyltin bromide (24). The product from the reaction with trimethyltin bromide is of particular interest

because it contains a chain of five tin atoms.

Dimethyltin-disodium reacted with dimethyltin with the formation of tetramethylditin-disodium (24).

$$(CH_3)_2SnNa_2 + (CH_3)_2Sn \longrightarrow Na(CH_3)_2SnSn(CH_3)_2Na$$

R_3PbM'

Organolead-sodium compounds were destroyed by both air and moisture. Thus, when a liquid ammonia solution of triphenyllead-sodium was allowed to react with air, hexaphenyldilead and lead oxide were produced in about equal amounts (25). Decomposition of triphenyllead-sodium in liquid ammonia by the addition of water gave mostly lead oxide, but decomposition by the addition of butyl alcohol gave mostly lead hydroxide (25).

Ammonium bromide destroyed organolead-sodium compounds as well as all other R_nMM' compounds. In the case of lead compounds, however, the destruction was slower and a stable hydride was not formed. Several attempts were made to prepare organolead hydrides by this method, but none was successful (25). Also, Foster, Dix and Gruntfest (26) studied the reaction of triphenyllead-sodium with ammonium bromide, and they proposed the formation of triphenyllead-ammonium.

Gilman and Bailie (25) found that several R_3PbNa compounds reacted with benzyl chloride and ethyl bromide to yield $R_3PbCH_2C_6H_5$ and $R_3PbC_2H_5$, respectively. Also, they found that

triphenyllead-sodium reacted with benzohydryl chloride to produce the expected triphenylbenzohydryllead.

Foster and co-workers (26) reported that triphenyllead-sodium reacted with methylene dichloride, in the absence of ammonia, to form a waxy solid from which no pure compound could be isolated. They found the molecular weight of the waxy solid to be 640 and mentioned that this value suggested the product might contain two triphenyllead groups. Therefore, they felt that this waxy material may have been crude methylenebis(triphenyllead).

Leeper (27) found that good yields of triphenylbenzyllead were formed when benzyl chloride was added to the lithium, sodium, potassium, rubidium, calcium, barium, or strontium derivatives of triphenyllead. He also found that the calcium and lithium derivatives of triethyllead reacted with benzyl chloride to give triethylbenzyllead.

Little can be said of the reactions of diorganolead-dimetal compounds, since they are the least stable of the compounds mentioned in this report. Some decomposition takes place during their reactions with any other material. As mentioned previously, the preparation of diphenyllead-dimetal compounds may result in the simultaneous formation of other organolead-metal compounds; therefore, the reactions mentioned here may not be reactions of pure diphenyllead-dimetal compounds. Ammonium bromide was added to diphenyllead-dilithium,

and a small yield of hexaphenyldilead was obtained, but no hydrogen was evolved (28). Diphenyllead-dilithium reacted with diphenyllead dibromide, but hexaphenyldilead, rather than the expected diphenyllead, was formed. Apparently, diphenyllead-dilithium reacted in a very complex manner with ethyl bromide because a mixture of tetraaethyllead, triethylphenyllead, diethyldiphenyllead and triphenylethyllead was produced (28).

EXPERIMENTAL

Cleavage of Symmetrical Organolead Compounds by Metals

It was found that triphenyllead-sodium could be prepared by the cleavage of tetraphenyllead with sodium. One experimental condition was varied at a time to find the set of conditions which would give a maximum yield of triphenyllead-sodium. Since triphenyllead-sodium could not be isolated as such, an excess of ethyl bromide was added, and the amount of triphenylethyllead formed was used as a measure of the amount of triphenyllead-sodium formed by the cleavage.

Conditions influencing cleavage of tetraphenyllead

The general procedure was to dissolve 0.022 g. atom of sodium in 15 cc. of liquid ammonia and to force this solution over into a stirred suspension of 5.15 g. (0.01 mole) of powdered tetraphenyllead in 20 cc. of ether. More ammonia, 5 cc., was used to wash over any sodium that did not dissolve in the 15 cc. of ammonia. The whole procedure was carried out in an atmosphere of dry nitrogen. The reaction was allowed to continue for six minutes before a solution of 5 cc. (0.056 mole) of ethyl bromide in 10 cc. of ether was added.

The ammonia was allowed to evaporate, the ether was distilled off, and the residue was extracted with hot methyl alcohol followed by hot benzene. Triphenylethyllead was obtained from the methyl alcohol and was recrystallized from fresh solvent. Tetraphenyllead was obtained from the benzene extract and was recrystallized from chloroform. Each organolead compound was identified by a melting point and a mixed melting point. Residues that were insoluble in hot organic solvents were dissolved in ammonium acetate, and the inorganic lead was precipitated as lead chromate by the addition of potassium dichromate. The per cent yields were based on the amount of tetraphenyllead added; in no case were they calculated on the basis of only that part of the tetraphenyllead which reacted.

Solvents

Two experiments were run according to the general procedure, and the average yields of products were 68% of triphenylethyllead (m.p. 44-45°), 13% of inorganic lead, and 13% of recovered tetraphenyllead (m.p. 223-224°).

Another set of two experiments was run as above with the following modifications: 100 cc. of ether was used in which to suspend the tetraphenyllead, and 75 cc. of ammonia was used to dissolve the sodium. In one case, the cleavage was allowed to continue for five minutes. The products were 82% triphenylethyllead (m.p. 44-45°) and a trace of inorganic lead.

In the other case, the cleavage was allowed to continue six minutes. The yields, in this case, were 83% of triphenylethyllead (m.p. 44-45°), 6% of inorganic lead, and 5% of recovered tetraphenyllead (m.p. 224-225°).

When these two sets of experiments were compared, it was noticed that the yield of triphenylethyllead was 15% higher when the cleavage was run in the more dilute solution.

Temperature

The general procedure was modified by the use of 100 cc. of ether and 75 cc. of ammonia, and the cleavage was run at -70° for one hour before the ethyl bromide was added. The yields of products were 47% of triphenylethyllead (m.p. 42-43°), a trace of inorganic lead,and 35% of tetraphenyllead (m.p. 224-225°).

An experiment, previously described in this report, was run with all other conditions the same, but the time and temperature of cleavage were six minutes and about -30°. In this case, the yields of triphenylethyllead and tetraphenyllead were 83% and 5%, respectively. When the results of these experiments were compared, it was seen that cooling the cleavage reaction to -70° was not advisable since it decreased the yield of triphenylethyllead 36%.

Amount of ethyl bromide for derivatization

A suspension of 0.0039 mole of tetraphenyllead in 100 cc. of liquid ammonia was stirred while 0.0081 g. atom of sodium was added. After ten minutes, 0.0066 mole (1.7 equivalents) of ethyl bromide was added. The ammonia was allowed to evaporate from the grey solution, and then the residue was worked up as mentioned in the general procedure. No triphenylethyllead could be found in the methyl alcohol solution, but there were indications of the presence of triphenyllead hydroxide. This triphenyllead hydroxide was precipitated by the addition of hydrochloric acid. Recrystallization of the precipitate from ethyl alcohol gave a yield of 1.48 g. (80%) of triphenyllead chloride (m.p. 202-204°). A mixed melting point with known triphenyllead chloride was not depressed. The other products isolated were 6% inorganic lead and 8% tetraphenyllead (m.p. 223-224°).

The fact to observe is that 1.7 equivalents of ethyl bromide gave no triphenylethyllead, but Apperson had found that a large excess of ethyl bromide (10 equivalents) gave a 90% yield of triphenylethyllead. The triphenyllead-sodium that Apperson used was prepared from hexaphenyldilead and sodium.

Different metals

These experiments were run under identical conditions and

in duplicate. The metals were added to a stirred suspension of 2.57 g. (0.005 mole) of tetraphenyllead in 150 cc. of liquid ammonia and allowed to react six minutes before 1.9 g. (0.015 mole) of benzyl chloride was added. After the ammonia evaporated, the solid residue was heated with several portions of hot methyl alcohol to extract the triphenylbenzyllead. The residue was then heated with hot chloroform to dissolve the tetraphenyllead. The organolead compounds were crystallized twice from their respective solvents. The experimental data are given in Table I.

Table I.

Metal	g. atoms of metal used	% yield of $(C_6H_5)_3PbCH_2C_6H_5$	% $(C_6H_5)_4Pb$ recovered
K	0.01	77	9
Na	0.01	81	2
Li	0.01	64	14
Ca	0.005	66	15
Sr	0.005	67	18
Ba	0.005	55	22

An attempt was made to cleave tetraphenyllead with magnesium. Magnesium turnings, 0.005 g. atom, were added to 150 cc. of liquid ammonia, and then 0.01 g. of ammonium bromide was added. The liquid ammonia did not turn blue, but

after three minutes, 2.57 g. (0.005 mole) of tetraphenyllead was added and the solution was allowed to stir for two hours. Although the solution had not changed in appearance, 1.9 g. of benzyl chloride was added and the reaction worked up in the usual way. No triphenylbenzyllead was found and 90% of the tetraphenyllead was recovered.

Presence of sodamide

Sodamide was a by-product of the cleavage of tetraphenyllead with sodium. When an organic halide was added to derivatize the triphenyllead-sodium, the sodamide reacted with the halide more rapidly than did the triphenyllead-sodium. This fact was shown by a comparison of the experiment given below with those in which the sodamide was removed.

Metallic sodium, 0.23 g. (0.01 g. atom), was added to a suspension of 2.57 g. (0.005 mole) of tetraphenyllead in 150 cc. of liquid ammonia, and the reaction was allowed to continue for six minutes before the addition of 0.7 g. (0.0055 mole) of benzyl chloride. A red color developed immediately but faded rapidly. When the reaction was worked up in the usual way, 7% of triphenylbenzyllead (m.p. 90-91°), 74% of inorganic lead, and 6% of tetraphenyllead (m.p. 223-224°) were obtained.

Removal of sodamide

Filtration. This experiment was run in the same way as the experiment above, but after six minutes were allowed for the cleavage, the reaction mixture was filtered through a sintered glass crucible before the 0.7 g. of benzyl chloride was added. When the mixture was worked up by the same method, 70% of triphenylbenzyllead (m.p. 90-91°), 7% of inorganic lead, and 4% of tetraphenyllead (m.p. 223-224°) were obtained. Removal of the sodamide increased the yield of triphenylbenzyllead 63% as can be seen by comparison of this experiment with the preceding one.

Addition of ammonium bromide. Ammonium bromide reacts readily with sodamide and more slowly with triphenyllead-sodium (25, 26). This experiment was run to show that ammonium bromide could be used to destroy the sodamide without destroying the triphenyllead-sodium.

A solution of triphenyllead-sodium in 150 cc. of liquid ammonia was made in the same way by the addition of 0.01 g. atom of sodium to 0.005 mole of tetraphenyllead. After six minutes were allowed for the cleavage, 0.49 g. (0.005 mole) of ammonium bromide was added, and one minute later 1.72 cc. (0.015 mole) of benzyl chloride was introduced. The solution did not become red. After the mixture was worked up in the usual way, 83% of triphenylbenzyllead (m.p. 90-92°), no inorganic lead, and 9% of tetraphenyllead (m.p. 222-223°) were

obtained.

In the experiment just described, an excess of benzyl chloride was used, but if the sodamide had been destroyed, an excess of benzyl chloride should not be necessary. Therefore, another experiment was run in the same way as just described; but slightly more ammonium bromide, 0.54 g. (0.0055 mole), was added and also less benzyl chloride, 0.63 cc. (0.0055 mole), was used. Again, no red color could be detected during the reaction with benzyl chloride. The yields of products were 80% of triphenylbenzyllead (m.p. 91-92°) and 12% of tetraphenyllead (m.p. 224-225°). This experiment shows that an excess of benzyl chloride is not necessary if the sodamide has been destroyed.

Addition of excess ammonium bromide. Tetraphenyllead was cleaved with sodium under the same conditions as used above; then 0.98 g. (0.01 mole) of ammonium bromide was added. One minute later 0.63 cc. (0.0055 mole) of benzyl chloride was introduced. Only 24% of triphenylbenzyllead (m.p. 89-90°), 43% of inorganic lead and 0.37 g. of a mixture of tetraphenyllead and hexaphenyldilead were obtained. Although the excess ammonium bromide had reacted only one minute, it had destroyed about one-half of the triphenyllead-sodium.

Time

Tetraphenyllead, 5.15 g. (0.01 mole), was cleaved

according to the general procedure (p. 49), but the amounts of solvents were changed to 75 cc. of ether and 75 cc. of liquid ammonia. The cleavage was allowed to continue for one, two, and five minutes to give 56, 55, and 55% of triphenylethyllead; 2, 11, and 3% of inorganic lead; and 17, 5, and 4% of tetraphenyllead, respectively. The cleavage of one phenyl group from tetraphenyllead was essentially complete after one minute, but the blue color of the sodium did not fade before three minutes of reaction.

Excess sodium

Four experiments were run under similar conditions, but in two of them cleavage was allowed to continue for six minutes. In the other two, cleavage was allowed to continue for two and three-quarters hours. The solution of 0.044 g. atom of sodium in 10 cc. of liquid ammonia was added rapidly to a stirred suspension of 0.01 mole of tetraphenyllead in 20 cc. of ether. Two successive 5 cc. portions of liquid ammonia were used to wash over the rest of the sodium. The reaction was allowed to continue for either six minutes or two and three-quarters hours before the addition of 5 cc. of ethyl bromide in 10 cc. of ether. After the ammonia evaporated, 30 cc. of ether was added. Then the solution was filtered, and the filtrate was washed successively with dilute nitric acid, dilute sodium carbonate solution, and finally with water.

The ether solution was evaporated, and the residue was extracted with hot methyl alcohol. Any remaining solids were extracted with hot benzene. The solids that were insoluble in the hot organic solvents were dissolved in the nitric acid wash solution, neutralized with ammonium hydroxide, acidified with acetic acid, and the inorganic lead precipitated by the addition of potassium dichromate.

The triphenylethyllead obtained from the methyl alcohol solution and the tetraphenyllead from the benzene solution were recrystallized from fresh solvents and identified by melting points and mixed melting points.

The average yields for the six-minute cleavages were 68% of triphenylethyllead, 2% of inorganic lead, and 16% of tetraphenyllead; while the yields of the same compounds for the two and three-quarters hours cleavages were 66%, 12%, and 1%, respectively. Therefore, the amount of triphenyllead-sodium remained constant over a few hours, even in the presence of excess sodium, but there was a decrease in the yield of tetraphenyllead and an increase in the yield of inorganic lead when a longer time was allowed for the cleavage.

Since excess sodium did not decrease the yield of triphenyllead-sodium, it should be satisfactory to add metallic sodium to a suspension of tetraphenyllead in the ammonia-ether mixed solvent. Two check experiments were run as described

above, but the metallic sodium was added directly to a suspension of tetraphenyllead in a mixture of ether and liquid ammonia. Also, the cleavage was allowed to continue for six hours before the ethyl bromide was added. When the reaction was worked up in the same way, the averages of the yields of products were 58% of triphenylethyllead (m.p. 40-41°), no tetraphenyllead, and 25% inorganic lead.

Another experiment was run under the same conditions, but 0.1 mole of tetraphenyllead and corresponding amounts of the other reagents were used. Also, this cleavage was allowed to proceed for only fifteen minutes before the ethyl bromide was added. The reaction product was worked up by the same general method, but the methyl alcohol soluble fraction was subjected to a reduced pressure distillation. The product distilled at 190-200° (4 mm.) with some decomposition. This boiling point was considerably above that reported for diethyldiphenyllead [170-175° (5 mm.)] (28). Also, all of the distillate solidified at room temperature, and triphenylethyllead would not crystallize even if only a small amount of diethyldiphenyllead was present (49). The melting point of the distillate was 47-48°, and on recrystallization it was changed to 42-43°, which is the reported value for triphenylethyllead (50). The

(49) Apperson, unpublished studies.
(50) Krause and Schmitz, Ber., 52, 2150 (1919).

yields of the products were 67% triphenylethyllead (m.p. 42-43°), 11% inorganic lead, and 8% tetraphenyllead (m.p. 223-224°).

The ether that was removed from the crude reaction product of this last run was very carefully fractionated to separate the benzene from the ether. Benzene was formed from the phenyl group cleaved from the tetraphenyllead. Di-n-butyl ether was added in the fractionation to force all of the benzene through the column. The crude benzene fraction (b.p. 76-78°) amounted to 4.5 cc. or a 50 per cent yield based on the removal of one phenyl group from tetraphenyllead. The crude benzene contained unsaturated hydrocarbons, since it decolorized appreciable amounts of bromine. This unsaturated compound was not cyclohexadiene-1,3, since no color was produced when the crude benzene was treated with ethyl alcohol and concentrated sulfuric acid (51). The refractive index (n_D^{21}) of the crude benzene was 1.4860, but the reported value (52) is 1.50137. A 3 cc. portion of the crude benzene absorbed 0.3 cc. of bromine; and the benzene that was distilled from the bromides had a refractive index of 1.5010. Therefore, the impurity was an unsaturated compound and probably a partially reduced benzene ring. This purified benzene was nitrated under the conditions

(51) Markownikoff, Ann., 302, 31 (1898).
(52) Brühl, ibid., 200, 139 (1880).

given by Shriner and Fuson (53). Recrystallization of the crude product from dilute alcohol gave m-dinitrobenzene (m.p. 87-88°), the identity of which was proved by a mixed melting point.

A comparison of the results from cleavage experiments in which four equivalents of sodium were used showed that the yield of triphenylethyllead was decreased, and the yield of inorganic lead was increased after six hours of cleavage.

The experiments described below were run with different amounts of sodium in attempts to cleave two phenyl groups from tetraphenyllead. In every case, the sodium was dissolved in 15 cc. of liquid ammonia and added to a stirred suspension of 5.15 g. (0.01 mole) of tetraphenyllead. The rest of the sodium was rinsed over with 5 cc. more of liquid ammonia. The reaction was allowed to continue in a nitrogen atmosphere, with stirring, for two and three-quarters hours before a solution of 5 cc. of ethyl bromide in 10 cc. of ether was added. The ether layer was evaporated after it had been washed quickly with dilute nitric acid, sodium bicarbonate, and water. The residue was extracted with methyl alcohol and with benzene. Inorganic materials were dissolved in the wash nitric acid, and the lead chromate was precipitated. The yields of products are averages from duplicate runs.

(53) Shriner and Fuson, "Identification of Organic Compounds", John Wiley and Sons, New York (1935) p. 139.

When 0.506 g. (0.022 g. atom) of sodium was used, the yields of products were 74% of triphenylethyllead (m.p. 40-41°), 3% of inorganic lead, and 4% of tetraphenyllead (m.p. 222-223°).

When 1.01 g. (0.044 g. atom) of sodium was added, the average yield of each product was 66% of triphenylethyllead (m.p. 40-41°), 12% of inorganic lead, and 1% of tetraphenyllead (m.p. 221-222°).

When 1.51 g. (0.066 g. atom) of sodium was used, a total of 40 cc. of liquid ammonia had to be added to dissolve the sodium. The yields of products were 57% of triphenylethyllead (m.p. 41-42°) and 22% of inorganic lead.

When 2.02 g. (0.088 g. atom) of sodium was added, it was also necessary to use 40 cc. of liquid ammonia. The yield of each product was 57% of triphenylethyllead (m.p. 40-41°) and 15% of inorganic lead.

Diethyldiphenyllead could be found as a product in none of the above experiments; so there was no definite evidence that two phenyl groups were cleaved from tetraphenyllead. However, since an increase in the amount of sodium caused a slight decrease in the yield of triphenylethyllead, it is conceivable that two phenyl groups may have been cleaved from the tetraphenyllead to a small extent.

Optimum conditions

The powdered tetraphenyllead and 100 equivalents of ether are placed in a three-necked flask provided with a stirrer, separatory funnel, and a four inch long, 10 mm. diameter glass T-tube stoppered at the top. The side arm of the T-tube is connected to a trap. Now, 270 equivalents of liquid ammonia are added to the contents of the flask. While this solution is stirred, 2.4 equivalents of sodium is added, piece by piece, through the T-tube, and five to ten minutes is allowed for the cleavage to become complete. The sodamide, formed during the cleavage, may be removed either by filtration or by the addition of one equivalent of ammonium bromide. However, it is not necessary to remove the sodamide if the triphenyllead-sodium is to be used for the preparation of a triphenylalkyllead compound. In this case, a solution of 5 equivalents of the alkyl halide in an equal volume of ether is added. The ammonia is allowed to evaporate and the mixture is worked up as described previously.

Conditions influencing cleavage of tetraethyllead

Solvents. Tetraethyllead, 6.46 g. (0.02 mole), was added to a solution of 0.92 g. (0.04 g. atom) of sodium in 100 cc. of liquid ammonia. The blue color did not fade out until after fourteen minutes of reaction; then 0.04 mole of

n-butyl bromide in 25 cc. of ether was added. When all of the ammonia had evaporated, water was added, and the organic layer was washed with dilute hydrochloric acid, dilute sodium bicarbonate and water. The ether solution was dried, the ether removed and the residue distilled under reduced pressure to yield 5.6 g. (80%) of triethyl-n-butyllead. All of the yields in this section were calculated on the basis of the amount of tetraethyllead added. The physical properties of the distillate were: b.p. 81-83° (5 mm.), n_D^{20} 1.5112, and d_4^{20} 1.5283. Redistillation of the organolead compound through the same fractionating column gave a distillate with a boiling point of 106-108° (13 mm.) and a refractive index (n_D^{20}) of 1.5122. These values check the reported values for triethyl-n-butyllead (54). Tetraethyllead was found to be only slightly soluble in liquid ammonia.

Toluene, 50 cc., was used to dissolve 6.46 g. (0.02 mole) of tetraethyllead; then a solution of 0.92 g. (0.04 g. atom) of sodium in 150 cc. of liquid ammonia was added. Six minutes were allowed for the cleavage to become complete before 5.48 g. (0.04 mole) of n-butyl bromide in 20 cc. of ether was added. The reaction was worked up in the same way as mentioned above. A yield of 6.2 g. (88%) triethyl-n-butyllead was obtained. The constants of this product were

(54) Grüttner and Krause, Ber., 50, 202 (1917).

b.p. 91-93° (8 mm.) and n_D^{20} 1.5121.

Ether, 50 cc., was used as a solvent for 6.4 g. (0.02 mole) of tetraethyllead. To this solution was added 0.92 g. (0.04 g. atom) of sodium in 150 cc. of liquid ammonia according to the procedure mentioned above. When the reaction was worked up in the same way, the yield of triethyl-n-butyllead was found to be 91%. The boiling point and refractive index (n_D^{20}) were 81-83° (5 mm.) and 1.5122, respectively. Other runs gave yields as high as 95% of triethyl-n-butyllead.

Cleavage was slower and less complete in liquid ammonia alone than in the cases where mixed solvents were used. The most complete cleavage was obtained when ether-ammonia solvent was used.

Temperature

A mixture of 150 cc. of liquid ammonia and 150 cc. of ether was used to dissolve 0.92 g. (0.04 g. atom) of sodium. The solution was then cooled in a bath of ether and solid carbon dioxide while 6.46 g. (0.02 mole) of tetraethyllead was added. The blue of the sodium solution was rapidly discharged, but the cleavage was allowed to continue for three minutes; then 5.48 g. (0.04 mole) of n-butyl bromide was added. All of these reactions were run in an atmosphere of nitrogen. The reaction mixture was worked up in the usual manner, and 6.7 g.

(95%) of triethyl-n-butyllead was obtained. The constants of the product were b.p. 82-84° (5 mm.) and n_D^{20} 1.5120.

When the reaction mixture was not cooled, but with all other conditions the same, a yield of 91% triethyl-n-butyllead was obtained. The boiling point and refractive index of this product were 81-83° (5 mm.) and 1.5123, respectively.

A lower temperature has no marked effect on the cleavage or derivatization reaction.

Amount of n-butyl bromide for derivatization

The same general procedure was used on the following sets of experiments. Tetraethyllead, 6.4 g. (0.02 mole), was dissolved in 150 cc. of ether, and 150 cc. of liquid ammonia was added. Sodium, 0.92 g. (0.04 g. atom), was then introduced and allowed to react for seven minutes before a definite amount of n-butyl bromide was added. A nitrogen atmosphere was employed during these reactions. After the liquid ammonia had evaporated, the reaction mixture was filtered; and the ether filtrate was washed successively with dilute hydrochloric acid, dilute sodium carbonate, and water. The organic layer was dried, the ether was removed and the residue was fractionated through a column of about ten theoretical plates.

One equivalent. In this run, 2.74 g. (0.02 mole) of n-butyl bromide was added to the solution of triethyllead-sodium

according to the general procedure described above. There were several differences between this and the other runs in this section when the reactions were worked up. First, the ether solution turned pink when it was being filtered. Second, the filtrate turned black immediately upon the addition of dilute hydrochloric acid. Third, decomposition of the organolead fraction took place during distillation. These three changes also took place when a solution of triethyllead-sodium was treated in the same way. These similarities indicated that one equivalent of n-butyl bromide may be insufficient to derivatize the triethyllead-sodium. This was emphasized by the isolation of a less pure triethyl-n-butyllead in a lower yield. The yield of triethyl-n-butyllead was 5.4 g. (77%), and although it was fractionated twice, the refractive index at 21° was 1.5152. This value did not agree well with the reported value (1.5120). The product had a density of 1.5272 at 21°.

One and one-half equivalents. This reaction was run according to the general procedure described at the first of this section, but this was a larger run and was done in a more concentrated solution. Tetraethyllead, 127.2 g. (0.4 mole), in 500 cc. of ether was added to a solution of 18.6 g. (0.81 g. atom) of sodium in 500 cc. of liquid ammonia. Later, 82.5 g. (0.6 mole), of n-butyl bromide in 75 cc. of ether was added. The yield of triethyl-n-butyllead was 125.1 g. (90%), and the

characteristics of this product were n_D^{21} 1.5125, b.p. 80-82° (4 mm.) and 104-106° (12 mm.).

Two equivalents. The same general procedure was followed and 5.48 g. (0.04 mole) of n-butyl bromide was added to derivatize the triethyllead-sodium. The product, which boiled steadily at 81-83°, was collected in two fractions. Since both fractions were found to have the same refractive index (n_D^{20} 1.5122), they were combined. The density (d_4^{20}) of the combined fractions was 1.5122, and the yield was 91%.

The cleavage was repeated in a larger run and in a more concentrated solution. Tetraethyllead, 127.2 g. (0.4 mole), in 500 cc. of ether was added in a slow stream to a solution of 18.6 g. (0.81 g. atom) of sodium in 500 cc. of liquid ammonia. The reaction was allowed to continue for ten minutes; then 109.1 g. (0.8 mole) of n-butyl bromide in 100 cc. of ether was added. When the product was worked up in the usual way, 131.5 g. (94%) of triethyl-n-butyllead was obtained. The boiling point and refractive index (n_D^{20}) of this product were 104-106° (12 mm.) and 1.5123, respectively.

Five equivalents. Another run was made according to the general procedure, but 20.5 g. (0.15 mole) of n-butyl bromide was added to derivatize the triethyllead-sodium. The yield of triethyl-n-butyllead was 10 g. (95%). The characteristics of this product were n_D^{21} 1.5125, b.p. 91-93° (8 mm.), and

106-107° (13 mm.). Since this was the first experiment of this set to be run, a lead analysis was also made on the product (55).

Anal. Calcd. for $C_{10}H_{24}Pb$: Pb, 59.0. Found: Pb, 58.6.

Different metals

Liquid ammonia, 150 cc., was used to dissolve the metal used for cleavage, and 50 cc. of toluene was added. Two minutes after the addition of 6.46 g. (0.02 mole) of tetraethyllead the solution lost the blue color and became slightly orange. Six minutes was allowed for the reaction to become complete before 5.48 g. (0.04 mole) of n-butyl bromide in 20 cc. of ether was added. The reaction mixture was worked up in the usual way.

When 0.8 g. (0.02 g. atom) of calcium was used as a cleaving agent, a 94% yield (6.6 g.) of triethyl-n-butyllead was obtained. The constants for the products were b.p. 91-93° (8 mm.) and n_D^{20} 1.5123.

When 0.28 g. (0.04 g. atom) of lithium was employed as a cleaving agent, a 94% yield of triethyl-n-butyllead was also obtained. The constants for the product were b.p. 91-93° (8 mm.) and n_D^{20} 1.5124.

(55) All lead analyses were carried out according to the method of Gilman and Robinson, J. Am. Chem. Soc., 50, 1714 (1928).

When 0.92 g. (0.04 g. atom) of sodium was used as a cleaving agent, an 88% yield (6.2 g.) of triethyl-n-butyllead was isolated. The constants for this product were found to be b.p. 89-91° (7 mm.) and n_D^{20} 1.5121.

Under these conditions there is no appreciable difference in the cleavage ability of these metals.

Removal of sodamide

Filtration. A solution of triethyllead-sodium in a mixture of ether and liquid ammonia was prepared by the addition of 12.92 g. (0.04 mole) of tetraethyllead in 50 cc. of ether to a solution of 1.84 g. (0.08 g. atom) of sodium in 50 cc. of liquid ammonia. The cleavage was allowed to continue for six minutes before the reaction mixture was filtered through glass wool. The filtrate was then treated with 5.4 g. (0.04 mole) of n-butyl bromide. After the ammonia had evaporated, the ether solution was washed with water, dried, evaporated, and distilled under reduced pressure. The main fraction boiled at 91-93° (8 mm.) and amounted to 11.8 g. (85%) of triethyl-n-butyllead. The lower yield was probably due to loss of triethyllead-sodium during filtration because there were no color changes or evidence of instability during distillation which would indicate incompletely derivatized triethyllead-sodium.

Addition of ammonium bromide. A solution of

triethyllead-sodium was made in the same manner as above; then instead of being filtered, the solution was treated with 3.92 g. (0.04 mole) of powdered dry ammonium bromide. The ammonium bromide changed the color of the solution to yellow, and then a brilliant red ring formed on the surface of the reaction mixture. Thirty seconds after the ammonium bromide was added, 10.96 g. (0.08 mole) of n-butyl bromide was introduced. A yellow color then developed in the solution, but by the time the ammonia evaporated, orange was the predominating color. Upon the addition of water, a light yellow precipitate formed. After filtration, the ether solution was washed thoroughly with water and worked up in the usual way to yield 8 g. (57%) of triethyl-n-butyllead and 0.53 g. (41%) of lead chromate. The boiling point and refractive index (n_D^{20}) of the triethyl-n-butyllead were 90-92° (8 mm.) and 1.5137, respectively.

Under ordinary conditions, it is not advisable to use either of these methods for the removal of sodamide. Instead, one should add enough organic halide to react with both the sodamide and triethyllead-sodium.

Excess metal

A solution of 6.46 g. (0.02 mole) of tetraethyllead in 50 cc. of toluene was added to 1.6 g. (0.04 g. atom) of calcium in 150 cc. of liquid ammonia. The reaction was allowed to continue for seventeen minutes in an atmosphere of nitrogen;

then a solution of 10.96 g. (0.08 mole) of n-butyl bromide in 40 cc. of ether was added. The ammonia was allowed to evaporate, and the resulting ether solution was washed successively with dilute acetic acid, dilute sodium hydroxide solution, and water. The organic layer was then dried and subjected to fractional distillation. The only organolead compound obtained was 6.1 g. (87%) of triethyl-n-butyllead. The boiling point was 90-94° (8 mm.), and the refractive index (n_D^{20}) was 1.5120. There was no evidence that two ethyl groups were cleaved from tetraethyllead under these conditions.

Conditions for more vigorous cleavage were used when 4.6 g. (0.2 g. atom) of sodium in 200 cc. of liquid ammonia was treated with a solution of 16.15 g. (0.05 mole) of tetraethyllead in 20 cc. of ether. The reaction was allowed to continue for two and one-half hours. By this time, most of the ammonia had evaporated; so 50 cc. more of liquid ammonia was introduced. Then 19 g. (0.2 mole) of methyl bromide in 20 cc. of ether was added very cautiously. The reaction was worked up in the same manner as described above. Two fractional distillations were necessary to separate the mixture into three main fractions. The first was 0.7 g. of an impure compound which boiled at 40-47° (16 mm.). The second was 2.15 g. of diethyldimethyllead or a 15% yield. The third was 5.5 g. of triethylmethyllead or a 36% yield. The observed constants for diethyldimethyllead were b.p. 54-56° (16 mm.),

n_D^{20} 1.5168 and d_4^{20} 1.7852. The observed characteristics of the triethylmethyllead were b.p. 70-72° (16 mm.), n_D^{24} 1.5153 and d_4^{23} 1.7122. These observed constants check the reported constants for both diethyldimethyllead (56) and triethylmethyllead (57).

Optimum conditions

A solution of 2.2 equivalents of sodium in 100 equivalents of liquid ammonia is made in a three-necked flask provided with a stirrer, separatory funnel, and a four inch long, 10 mm. diameter glass T-tube stoppered at the top. The side arm of the T-tube is connected to a trap. A solution of tetraethyllead in 20 equivalents of sodium dried ether is added rapidly to the stirred solution of sodium. After six minutes, the solution may be filtered to remove the excess sodamide; however, if the solution of triethyllead-sodium is to be used for the preparation of an unsymmetrical organolead compound, it is not necessary to remove the sodamide. In this case, a solution of 1.5 equivalents of the alkyl halide in an equal volume of ether is added. The reaction is worked up as described previously.

(56) Moller and Pfeiffer, Ber., 49, 2441 (1916).
(57) Grüttner and Krause, Ibid., 49, 1125 (1916).

Cleavage of Organolead Compounds in Inert Solvents

With the binary system ($Mg + MgI_2$)

An attempt was made to cleave triphenylbenzyllead with the binary system of Gomberg and Bachmann (58), but apparently only a redistribution reaction took place. Powdered magnesium, 1 g. (0.042 g. atom), was covered with 25 cc. of ether, and 1.5 g. (0.0118 g. atom) of iodine was added and allowed to react until the solution became colorless. To this solution, which contained magnesious iodide, was added 2.65 g. (0.005 mole) of triphenylbenzyllead in 50 cc. of benzene. The solution became slightly green, but all of the color tests with Michler ketone were negative. After forty-one hours of reaction, an excess of ethyl bromide was added and allowed to react fifteen minutes before the solution was filtered. The filtrate was evaporated and the residue extracted with hot ethyl alcohol. Some decomposition took place in the hot alcohol solution. When the alcohol solution was cooled, 1 g. (38%) of triphenylbenzyllead (m.p. 93-94°) was obtained. The residue left from the hot alcohol extraction was crystallized from chloroform to yield 0.3 g. (11.5%) of tetraphenyllead (m.p. 223-224°). The identity of each of these compounds was

(58) Gomberg and Bachmann, J. Am. Chem. Soc., 49, 2584 (1927).

proved by a mixed melting point determination.

Since tetraphenyllead and unstable organolead compounds were found as products, it is probable that a redistribution reaction took place.

With sodium amalgam

Two attempts were made to cleave triphenylbenzyllead with sodium amalgam. In both cases, a solution of 2.65 g. (0.005 mole) of triphenylbenzyllead in 50 cc. of ether was stirred with 0.35 g. (0.015 g. atom) of sodium in 26 g. of mercury. One reaction was allowed to go five and one-half hours at room temperature before 2.16 g. (0.02 mole) of ethyl bromide in 10 cc. of ether was added. The ether solution was evaporated, and the residue was crystallized from methyl alcohol. The only product that could be isolated was 2.25 g. (86%) of triphenylbenzyllead (m.p. 92-93°). The other reaction was refluxed twenty-eight hours before the ethyl bromide was added. Again, 2.26 g. (86%) of triphenylbenzyllead (m.p. 92-93°) was the only product found.

With sodium

A solution of 1.4 g. (0.06 g. atom) of sodium in liquid ammonia was made and the ammonia was allowed to evaporate to

form a thin layer of sodium on the inside of the flask. Then, 50 cc. of ether and 8.3 g. (0.025 mole) of tetraethyllead were added, and the mixture was stirred for two hours. The surface of the sodium became dark, but apparently there was no appreciable reaction. Dry ammonia gas was introduced above the liquid; then the ether began to reflux and a gas was evolved. The reaction flask was cooled in an ice-salt cooling mixture. The color of the solution became yellow and then a very deep red. Methyl iodide, 8.5 g., was introduced and allowed to react five minutes before ethyl alcohol was added. The reaction mixture was filtered to separate 3.2 g. (28%) of lead iodide. The filtrate was subjected to fractional distillation. The crude organolead distillate was refractionated, but only 1.4 g. (18%) of triethylmethyllead was obtained. The constants observed for the product were b.p. 75-78° (17 mm.), n_D^{24} 1.5169, and d_4^{24} 1.7092 (55).

This experiment was repeated, but this time 16.6 g. (0.05 mole) of tetraethyllead, 2.3 g. (0.1 g. atom) of sodium, and 100 cc. of ether were used. The reaction was kept at -10° from the start of the introduction of ammonia. Also, 14.2 g. (0.1 mole) of methyl iodide was added before the solution became red. The reaction mixture was worked up in the same way to yield 3.37 g. (15%) of lead iodide and 7.3 g. (47%) of triethylmethyllead. The latter product had the following constants: b.p. 72-74° (16 mm.), n_D^{24} 1.5150, and d_4^{24} 1.7120.

Reaction of Organolead-sodium with Organic Halides

Triphenyllead-sodium

Ethylene dibromide

Triphenyllead-sodium was prepared by the addition of a slight excess of sodium to a suspension of 2.83 g. (0.005 mole) of triphenyllead iodide in 150 cc. of liquid ammonia. Then a solution of 1.03 g. (0.0055 mole) of ethylene dibromide in 10 cc. of ether was added. After evaporation of the ammonia had taken place, water was added, and the mixture was filtered. An attempt was made to extract unsymmetrical organolead compounds by the use of hot methyl alcohol, but none of the residue dissolved. The residue was then extracted with chloroform, and the solution was concentrated and cooled. When methyl alcohol was added to the cold solution, 1.75 g. (80%) of hexaphenyldilead precipitated. The product darkened at 172° and melted at 225-226°.

An attempt was made to use a modification of this procedure as a rapid method for the preparation of hexaphenyldilead. Tetraphenyllead, 5.15 g. (0.01 mole), was cleaved by 0.5 g. (0.022 g. atom) of sodium in a mixture of 75 cc. of liquid ammonia and 50 cc. of ether. The reaction was allowed to continue for ten minutes before 4.14 g. (0.022 mole) of

ethylene dibromide in 10 cc. of ether was added. The addition had to be done carefully until the excess sodium had been destroyed. The ammonia and ether were evaporated; then the residue was extracted with chloroform. The chloroform solution was concentrated, and the hexaphenyldilead was forced out of solution by the addition of methyl alcohol. The yield of hexaphenyldilead was 2.5 g. (57%). A melting point sample darkened at 170° and melted at 224-225°. When the experiment was repeated, 2.58 g. (59%) of hexaphenyldilead was obtained. A lead analysis proved the product was pure.

Anal. Calcd. for $C_{36}H_{30}Pb_2$: Pb, 47.3. Found: Pb, 46.9, 47.0.

The presence of a large excess of ethylene dibromide during its reaction with triphenyllead-sodium may lead to the production of either triphenyllead bromide or triphenyl-β-bromoethyllead. Therefore, a solution of triphenyllead-sodium in 75 cc. of liquid ammonia and 50 cc. of ether was made by the cleavage of 5.15 g. (0.01 mole) of tetraphenyllead with 0.5 g. (0.022 g. atom) of sodium. This solution of triphenyllead-sodium was slowly forced over into a stirred solution of 10 cc. of ethylene dibromide in 20 cc. of ether. The ammonia was allowed to evaporate, and the residue was subjected to steam-distillation. The nonvolatile portion was extracted with hot methyl alcohol followed by hot chloroform. The methyl alcohol solution contained a compound that was very soluble but which had no definite melting point. These properties are

remindful of triphenyllead hydroxide; so the alcohol solution was treated with dilute hydrochloric acid. Immediately a white precipitate was formed which, when recrystallized from ethyl alcohol, amounted to 0.11 g. (2%) triphenyllead chloride (m.p. 204-205°). A mixed melting point with an authentic specimen of triphenyllead chloride was not depressed. The chloroform solution was concentrated and cooled to yield 0.31 g. (6%) of tetraphenyllead (m.p. 223-224°). Methyl alcohol was then added to the chloroform. This treatment caused 1.33 g. (34%) of hexaphenyldilead to precipitate.

p-Chlorotoluene

All of the reactions between triphenyllead-sodium and aryl halides described in this section were run under similar conditions and worked up according to the same general directions. These general directions were to add 4.73 g. (0.01 mole) of triphenyllead chloride to 100 cc. of liquid ammonia in a 250 cc. three-necked flask and then to introduce 0.5 g. (0.022 g. atom) of metallic sodium. After six minutes, 25 cc. of ether and a definite amount of the aryl halide were added. The reaction was allowed to continue for various lengths of time before the mixture was hydrolyzed. The mixture was steam-distilled, and the nonvolatile portion was extracted successively with hot ethyl alcohol, chloroform and ammonium acetate. All of the products were identified by a melting

point and a mixed melting point determination. The yields were based on the amount of tetraphenyllead added.

After 2.85 cc. (0.024 mole) of p-chlorotoluene was added to the solution of triphenyllead-sodium, the reaction was allowed to continue for thirty-six hours. The mixture was worked up as outlined above, but the alcohol solution contained no organolead compound. The mixture that was soluble in chloroform could not be separated by fractional crystallization from chloroform, benzene or petroleum ether. The yield of inorganic lead was 60%.

p-Bromotoluene

The general directions were followed in a reaction of triphenyllead-sodium with 2.95 cc. (0.024 mole) of p-bromotoluene. The reaction was allowed to continue for thirty-six hours before water was added. Only a tar was obtained from the alcohol extract and no pure compound could be isolated from it. A small amount of dark material was obtained from the chloroform solution, but it could not be purified by crystallization from chloroform, ether, or acetone. The yield of inorganic lead was 53%.

p-Iodotoluene

A solution of triphenyllead-sodium was treated with 5.23 g. (0.024 mole) of p-iodotoluene and was allowed to react for

eight hours in one run and for twenty-three hours in another run. The reaction was worked up as described in the general directions, and after many recrystallizations, the chloroform soluble fraction was separated into tetraphenyllead and a compound that melted at 115-119°. The latter compound was proved to be triphenyl-p-tolyllead, since a mixed melting point with an authentic specimen was not depressed. The yields of products from the eight hour run were 0.2 g. (4%) of triphenyl-p-tolyllead (m.p. 115-119°) and 0.1 g. (3%) of tetraphenyllead (m.p. 222-224°). The yields of products from the twenty-three hour run were 0.25 g. (5%) of triphenyl-p-tolyllead (m.p. 115-119°) and 0.3 g. (8%) of tetraphenyllead (m.p. 223-224°). In spite of the five recrystallizations, the triphenyl-p-tolyllead was not pure, since the observed melting point was 6 to 10° lower than the melting point which has been reported for this compound (59).

Methyl p-bromobenzoate

The solution of triphenyllead-sodium was treated with 2.15 g. (0.01 mole) of methyl p-bromobenzoate and was allowed to react for twenty-four hours. The reaction was worked up as mentioned above, but the residue from the alcohol solution was extracted with hot water. When the water solution cooled,

(59) Krause and Schmitz, Ber., 52, 2150 (1919).

crystals of an amide formed. All aqueous solutions were then acidified and extracted with ether. The ether was evaporated, and the residue was recrystallized from methyl alcohol. The product was 1.1 g. (55%) of p-bromobenzamide (m.p. 196-197°). The identity of the product was confirmed by a mixed melting point with an authentic specimen of p-bromobenzamide. No pure organolead compound could be isolated as a product of this reaction.

p-Iodonitrobenzene

The reaction between triphenyllead-sodium and 2.5 g. (0.01 mole) of p-iodonitrobenzene was carried out according to the general directions, but a benzene solution of p-iodonitrobenzene was added to the triphenyllead-sodium. A very intense red color developed in the solution, but the reaction was allowed to continue for twenty-four hours. The only organolead compound isolated in the pure state was 3.3 g. (60%) of hexaphenyldilead.

This reaction was repeated, but 8.34 g. (0.034 mole) of solid p-iodonitrobenzene was added to the solution of triphenyllead-sodium. Again, the red color developed, and the reaction was allowed to continue for twenty-four hours. This time, 1.85 g. (43%) of hexaphenyldilead, 0.3 g. (8%) of tetraphenyllead, and 0.25 g. (8%) of lead chromate were obtained.

2,4-Dinitrochlorobenzene

A solution of triphenyllead-sodium, prepared according to the general directions, was treated with 2.03 g. (0.01 mole) of 2,4-dinitrochlorobenzene. An intense red color developed immediately, and then it changed to a violet color. Most of the products dissolved in the hot alcohol, but when the solution was cooled, only a tar could be obtained. No pure compounds could be isolated from this reaction. When liquid ammonia was added to 2,4-dinitrochlorobenzene, a red color developed and was soon replaced by a violet color. However, upon evaporation of the ammonia, the melting point of the 2,4-dinitrochlorobenzene was unchanged.

Triethyllead-sodium

Methyl bromide

Tetraethyllead, 12.92 g. (0.04 mole), was dissolved in 50 cc. of ether, and added to a solution of 0.56 g. (0.08 g. atom) of lithium in 75 cc. of liquid ammonia while the reaction was cooled in an acetone-solid carbon dioxide bath. A nitrogen atmosphere was used. After ten minutes of cleavage, 7.6 g. (0.08 mole) of methyl bromide in 20 cc. of ether was added. The ether solution, remaining after evaporation of the ammonia, was washed several times with water, dried, the

ether fractionated off and the residual oil subjected to reduced pressure distillation. The yield of triethylmethyllead was 10.34 g. (85%) and its identity was proved by the constants b.p. 75-76° (18 mm.), n_D^{25} 1.5153, and d_4^{20} 1.7120. These constants check those reported for triethylmethyllead (57).

Benzyl chloride

Sodium, 6.9 g. (0.3 g. atom), was dissolved in 225 cc. of liquid ammonia, and a solution of 49.4 g. (0.15 mole) of tetraethyllead in 225 cc. of ether was added rapidly. A solution of 37.8 g. (0.3 mole) of benzyl chloride in 35 cc. of ether was then added. At this stage red streamers extended through the thick grey solution. The red color seemed to originate from the precipitate in the bottom of the flask and then to fade as it went through the solution. After two hours, water was added; and the ether solution was washed successively with dilute acetic acid, dilute sodium hydroxide solution and water. The organic layer was dried over sodium sulfate and the ether removed. Crystals began to form in the residual oil; so it was cooled and filtered. The solid weighed 4.8 g. and melted at 111-122°. Two recrystallizations from petroleum ether (b.p. 75-115°) gave crystals with a melting point of 123.5-124°. A mixed melting point with an authentic specimen of stilbene was not depressed. The oil

from the filtrate above was distilled at 4 mm. Some decomposition took place, but 41 g. of distillate, boiling at 115-120°, was obtained. Upon redistillation, decomposition again took place, giving only low boiling fractions. No triethylbenzyllead could be obtained. This experiment was checked on a smaller run with the same results.

It was felt that the sodamide may have interfered with the derivatization; so the experiment was repeated and the triethyllead-sodium was filtered to remove the sodamide. Sodium, 0.3 g. atom, was dissolved in 225 cc. of liquid ammonia, and 0.15 mole of tetraethyllead in 225 cc. of ether was added. The solution was filtered through a sintered glass crucible, and to it was added 0.177 mole of benzyl chloride. No red color developed during this reaction. The mixture was worked up in the same way as above, and again, decomposition took place during the distillation. The fraction that boiled at 125-128° (4 mm.) was collected and redistilled, but only 5.6 g. (10%) of triethylbenzyllead was obtained. The observed boiling point was 150-152° (13 mm.), and the density (d_4^{23}) was 1.5381. These values check the reported values (60).

(60) Grüttner and Grüttner, Ber., 51, 1293 (1918).

t-Butyl bromide

An ether solution of 12.92 g. (0.04 mole) of tetraethyllead was rapidly added to 1.84 g. (0.08 g. atom) of sodium in 50 cc. of liquid ammonia. Adding 10.96 g. (0.08 mole) of t-butyl bromide caused no color change. Usually, the color changed from a green to a light grey during derivatization. After five hours, the solution was red with an orange and black precipitate on the sides of the flask. The addition of water caused a vigorous reaction, and the solution turned to a dark red, then quickly to a black amorphous mass. The mixture was filtered, and the filtrate was washed several times with water, dried and worked up in the usual manner. Distillation was accompanied by considerable decomposition; so it was necessary to carry out two more fractional distillations before the product could be identified. Tetraethyllead, 4 g., was the only compound that could be isolated in the pure state. The observed constants were b.p. 60-63° (6 mm.), n_D^{18} 1.5208, and d_4^{18} 1.6584. These values check those reported for tetraethyllead (61).

Dehydrohalogenation takes place much more readily with t-butyl bromide than with n-butyl bromide, and sodamide is a reagent that causes dehydrohalogenation (62). It may be that

(61) Grüttner and Krause, ibid., 49, 1415 (1916).
(62) Bergstrom and Fernelius, Chem. Rev., 12, 43 (1933).

ammonium bromide was formed from the dehydrohalogenation of the t-butyl bromide and that it destroyed the triethyllead-sodium. To test this idea, 32.3 g. (0.1 mole) of tetraethyllead in 150 cc. of ether was added to 4.6 g. (0.2 g. atom) of sodium in 150 cc. of liquid ammonia, and 27.4 g. (0.2 mole) of t-butyl bromide in 20 cc. of ether was added. After the reaction was allowed to take place four minutes, a red color developed; then 21.6 g. (0.2 mole) of ethyl bromide was added. The reaction was worked up in the usual way and gave 30.5 g. of an oil boiling at 59-61° (6 mm.). Other constants were d_4^{18} 1.6584 and n_D^{18} 1.5208. These constants proved the liquid was tetraethyllead since they check the reported values for this compound (61). The yield of tetraethyllead was 95%.

The same amounts of reactants were mixed in the same way as above, but this time the t-butyl bromide was allowed to react four hours with the triethyllead-sodium at the temperature of an acetone-solid carbon dioxide bath and in an atmosphere of nitrogen. At the end of four hours the solution was red and contained some black precipitate. The 0.2 mole of ethyl bromide was then added, and the reaction worked up in the same way. Considerable decomposition took place during fractional distillation. The only product isolated was 9.7 g. (30%) of tetraethyllead boiling at 60-63° (6 mm.). Two more fractionational distillations were necessary to bring the refractive index up to 1.5191 at 18°. No triethyl-t-butyllead

could be isolated.

Iodobenzene

Tetraethyllead, 32.3 g. (0.1 mole), was dissolved in 50 cc. of ether and 75 cc. of liquid ammonia; then 4.6 g. (0.2 g. atom) of sodium was added piece by piece. The sodium dissolved slowly; so 50 cc. more of liquid ammonia was added, and fifteen minutes allowed for solution to take place. A solution of 40.8 g. (0.2 mole) of iodobenzene in 20 cc. of ether was added, and, three minutes afterward, a red color developed. The reaction was allowed to continue twenty minutes before the addition of 11 cc. of n-butyl bromide. When the ammonia had evaporated, water was added, and the ether layer washed quickly with dilute hydrochloric acid, dilute sodium bicarbonate solution, and water. The organic layer was dried and subjected to fractional distillation. Decomposition took place during distillation and gave 13 g. of liquid boiling at 61-64° (6 mm.) which was probably tetraethyllead. The other fraction boiled at 127-131° (7 mm.) and 135-137° (12 mm.) and amounted to 5.6 g. (15% yield) of triethylphenyllead. The unsymmetrical organolead compound was not absolutely pure as shown by the refractive index (n_D^{20}) of 1.5532. The reported constants for triethylphenyllead are b.p. 135° (13 mm.) and n_D^{20} 1.5762 (60).

The experiment was repeated under slightly different conditions as 45 g. (0.139 mole) of tetraethyllead in 150 cc.

of ether was added rapidly to a solution of 6.4 g. (0.278 g. atom) of sodium in 150 cc. of liquid ammonia. A solution of 56.8 g. (0.278 mole) of iodobenzene in 60 cc. of ether was then added. There was a solid in the bottom of the flask which began to turn to a mushy consistency after ninety minutes of reaction; so water was added. The mushy material solidified during a vigorous evolution of a gas. The solution was filtered, and the solid washed thoroughly with ether to give white crystals which melted at 100-102°. The crystals burned with a colorless flame and contained lead and iodine. A small amount of the precipitate was dissolved in chloroform and was forced out of solution by the addition of petroleum ether. In attempts to repeat this crystallization only an oil could be obtained. Also, when other solvents were used the material always separated as an oil. The melting point of the purified crystals was 100-101.5°. The melting point does not agree with that of any known compounds which may be expected to be formed. The crude material was powdered and washed with water and with ether. The powder was dried, and a lead determination was made on this crude sample.
Anal. Calcd. for $[(C_2H_5)_3PbI]_2 \cdot (C_2H_5)_3Pb$: Pb, 54.7. Found: Pb, 55.9 and 55.7.

When the ether solution was worked up in the usual way, a small amount of high boiling material was found, but no pure fraction could be obtained.

Bromobenzene

Abbott (63) had found that bromobenzene reacted with triethyllead-sodium to give satisfactory yields of triethylphenyllead; so an experiment was run the same as above, but 0.278 mole of bromobenzene, instead of iodobenzene, was used for the derivatization. In this case, the reaction was allowed to go four hours. No precipitate formed upon the addition of water. A good yield, 39.7 g. (77%), of triethylphenyllead was obtained and was identified by the constants b.p. 137-140° (13 mm.), n_D^{20} 1.5752, and d_4^{21} 1.5915.

Allyl chloride

A solution of 49.4 g. (0.15 mole) of tetraethyllead in 225 cc. of dry ether was added rapidly to 6.9 g. (0.3 g. atom) of sodium in 225 cc. of liquid ammonia. To this mixture, 23 g. (0.3 mole) of allyl chloride in 25 cc. of ether was added dropwise. There was a very vigorous reaction, and a purple color developed, which lasted until all of the alkyl halide had been added. Water was added after the ammonia had evaporated, and the ether layer was washed successively with acetic acid, sodium hydroxide solution, and water. The oil, left after the ether was dried and removed, was fractionated to give 36.2 g. (72%) of triethylallyllead as proved by the

(63) R. K. Abbott, unpublished studies.

constants b.p. 85-86° (8 mm.), n_D^{22} 1.5410, and d_4^{23} 1.6056. These values check those reported for this compound (64). A check run gave a 71% yield of triethylallyllead.

s-Butyl bromide

A solution of triethyllead-sodium was made in the same way from 49.4 g. (0.15 mole) of tetraethyllead in 225 cc. of ether and 6.9 g. (0.3 g. atom) of sodium in 225 cc. of liquid ammonia. Derivatization was accomplished by the use of 41.1 g. (0.3 mole) of s-butyl bromide. The alkyl halide was added rather rapidly, but the green color did not fade rapidly, the solution did not boil as vigorously as usual and did not become thick immediately. These changes did take place in ten minutes, but the fact that they take place more slowly shows that s-butyl bromide reacts less rapidly than n-butyl bromide with triethyllead-sodium. The product was isolated in the usual manner to obtain 43.2 g. (82%) of triethyl-s-butyllead. The observed constants were b.p. 108-109° (15 mm.), n_D^{20} 1.5190, and d_4^{20} 1.5318. These constants check those reported for this compound (65, 66).

(64) Grüttner and Krause, Ann., 415, 338 (1918).
(65) Gilman, Sweeney and Robinson, Rec. trav. chim., 49, 205 (1930).
(66) Grüttner and Krause, Ber., 50, 574 (1917).

Trimethyllead-sodium

Bromobenzene

A solution of 38.7 g. (0.15 mole) of tetramethyllead* in 150 cc. of ether was added, in a slow stream, to a solution of 6.9 g. (0.3 g. atom) of sodium in 150 cc. of liquid ammonia. The reaction was quite vigorous, but a period of ten minutes was allowed for the reaction to come to completion. Then, 47.1 g. (0.3 mole) of bromobenzene in 60 cc. of ether was added to this brown solution of trimethyllead-sodium. The reaction was allowed to take place in a nitrogen atmosphere for thirty hours; then 10 cc. of ethyl bromide was added. Since there was no apparent reaction with the ethyl bromide, water was added and the mixture was worked up in the usual manner. The product was fractionally distilled twice and gave a yield of 20 g. (40%) of trimethylphenyllead. A check run gave a yield of 21.2 g. (43%). The boiling point of the product was 68-69° (3.5 mm.), and the refractive index at 20° was 1.5826. Since the boiling point did not agree with the one reported for this compound [77-78° (3 mm.)] (67), a lead analysis was run on the product.

* Kindly provided by Dr. G. Calingaert of the Ethyl Gasoline Corporation.

(67) Calingaert, Beatty and Soroos, J. Am. Chem. Soc., 62, 1099 (1940).

Anal. Calcd. for $C_9H_{14}Pb$: Pb, 62.9. Found: Pb, 62.8 and 62.7.

Also, 7 g. of a fraction boiling at 34-82° (120 mm.) was obtained during the fractionation of each run. These fractions were combined and refractionated to recover 10 g. (13%) of tetramethyllead. The constants of this product were b.p. 108-109°, d_4^{20} 1.9960, and n_D^{20} 1.5126, and they agreed well with the reported constants (62).

Preferential Cleavage of Organolead Compounds

The same directions were used for all of the preferential cleavages mentioned below. In this general method, a three-necked flask containing 180 cc. of liquid ammonia was cooled to -70°, and the whole system was flushed out with nitrogen. A definite amount of the metal was then dissolved in the liquid ammonia. To this solution was added a mixture of 0.1 mole of the unsymmetrical organolead compound dissolved in 126 cc. of dry ether. The reaction was allowed to continue for six minutes; then 0.2 mole of an appropriate alkyl halide in 20 cc. of ether was added to derivatize the organolead-metal compounds. The cooling bath was then removed, and the ammonia was allowed to evaporate. Water was added, and the ether layer was washed with dilute acetic acid, dilute sodium hydroxide solution, and water. After the ether layer was

dried over sodium sulfate, the ether was removed by distillation. The oily residue was then fractionally distilled through a column of about ten theoretical plates. The yield of each fraction was taken as the total amount of material collected from a temperature midway between the true boiling point and the boiling point of the next lighter compound to a temperature midway between the true boiling point and the boiling point of the next heavier compound. Each fraction was redistilled through the column, and the midportion was saved for analysis and for the determination of the physical constants. The yields were based on the total amount of unsymmetrical organolead compound added. Check runs were made in every case except in the cleavage of triethylmethyllead and triethyl-s-butyllead.

Triethyl-n-butyllead

Cleavage by different metals

Triethyl-n-butyllead was cleaved by calcium, lithium, and sodium to determine if one metal showed more of a preferential cleavage than another. In each case, 35.1 g. (0.1 mole) of triethyl-n-butyllead was used. Methyl bromide, 19 g. (0.2 mole), was introduced to derivatize the organolead—sodium compounds. The products isolated were triethylmethyllead, diethyl-n-butylmethyllead, and recovered

triethyl-n-butyllead. The physical constants for diethyl-n-butylmethyllead have not been published; so this product was identified as described later. The physical constants that have been reported for the other two compounds are: for triethylmethyllead, b.p. 70-70.5° (16 mm.), $n_D^{24.3}$ 1.5158, and $d_4^{23.2}$ 1.7124 (57); and for triethyl-n-butyllead, b.p. 108° (13 mm.), n_D^{21} 1.5120, and $d_4^{20.8}$ 1.5285 (54). Earlier in this report, the boiling point of triethyl-n-butyllead was reported as being 91-93° (8 mm.) and 81-83° (5 mm.).

Calcium. The reaction was run as described above using 4 g. (0.1 g. atom) of calcium. In two runs the yields of triethylmethyllead were 4.5 g. (14.5%) and 4.6 g. (15%), and the yields of diethyl-n-butylmethyllead were 14.3 g. (42.5%) and 15.6 g. (46.5%). The amounts of recovered triethyl-n-butyllead were 11.2 g. (32%) and 8.8 g. (25%). The physical constants for the three products were as follows: for triethylmethyllead, b.p. 71° (16 mm.), n_D^{24} 1.5150, and d_4^{23} 1.7114; for diethyl-n-butylmethyllead, b.p. 67° (5 mm.), n_D^{20} 1.5125, and d_4^{20} 1.5817; and for triethyl-n-butyllead, b.p. 91° (8 mm.), n_D^{20} 1.5122, and d_4^{21} 1.5290.

Lithium. When 1.38 g. (0.2 g. atom) of lithium was used as a cleaving agent, the yields of triethylmethyllead in two runs were 6.2 g. (20%) and 6.8 g. (22%); and the yields of diethyl-n-butylmethyllead were 19.8 g. (59%) and 19.4 g. (58%). The recovered triethyl-n-butyllead was 2.9 g. (8%) and 3.6 g.

(10%). The physical constants for the products were as follows: for triethylmethyllead, b.p. 44° (6 mm.) and n_D^{24} 1.5152; for diethyl-n-butylmethyllead, b.p. 69° (6 mm.), and n_D^{20} 1.5122; and for triethyl-n-butyllead, b.p. 89° (6 mm.), and n_D^{20} 1.5123.

Sodium. The experiment was run with 4.6 g. (0.2 g. atom) of sodium; and the yields of products were triethylmethyllead, 7.5 g. (24%) and 8.8 g. (28%); diethyl-n-butylmethyllead, 19.2 g. (57%) and 17.5 g. (52%); triethyl-n-butyllead, 2.8 g. (8%) and 4.2 g. (12%). The constants on each pure fraction were triethylmethyllead, b.p. 41° (4 mm.) and n_D^{24} 1.5153; diethyl-n-butylmethyllead, b.p. 66° (5 mm.) and n_D^{20} 1.5125; and triethyl-n-butyllead, b.p. 89° (6 mm.) and n_D^{20} 1.5124.

Identification of diethyl-n-butylmethyllead

All of the products were identified by boiling point, refractive index, and density. These figures are not reported for diethyl-n-butylmethyllead; so this compound was prepared by a standard procedure and the constants were determined for it. Triethyl-n-butyllead, 35.1 g. (0.1 mole), was cleaved by the introduction of hydrogen chloride over an ether solution of the organolead compound until a white precipitate began to form. Apparently diethyl-n-butyllead chloride was rather soluble in ether. The reaction mixture was filtered, and the filtrate was evaporated to a mushy consistency. More ether

was added and the mixture was again distilled. An excess of an ether solution of methylmagnesium bromide was added and refluxed for ten minutes. The reaction was hydrolyzed with iced ammonium chloride; then the ether solution was washed with dilute acetic acid, dilute sodium hydroxide solution, and water. After the organic layer was dried, the ether was distilled off and the residue fractionated three times through an efficient column. The physical constants of the main fraction, diethyl-n-butylmethyllead, were b.p. 80° (7 mm.) and 55° (3 mm.), n_D^{20} 1.5118, and d_4^{20} 1.5827.

Anal. Calcd. for $C_9H_{22}Pb$: Pb, 61.42. Found: Pb, 61.17, 61.21.

Triethylallyllead

Cleavage by sodium

The general method was applied to the cleavage of 33.5 g. (0.1 mole) of triethylallyllead by 4.6 g. (0.2 g. atom) of sodium. The reaction mixture developed a dark red color, but the solution became yellow after the 19 g. (0.2 mole) of methyl bromide was added. Some inorganic lead compounds were formed in this reaction and were isolated as lead chromate. The yields of lead chromate from two runs were 2.75 g. (8.5%) and 3.24 g. (10%). The yields of triethylmethyllead were 17.8 g. (58%) and 21 g. (68%). During the fractional distillation,

the boiling point became steady for a short time at 84° (15 mm.). This was approximately the temperature at which one would expect diethylallylmethyllead to boil. There was 1.5 g. of this impure fraction in one run and 0.6 g. in another. The yields of diethylallylmethyllead, then, were not more than 5% and 2%.

Since triethyllead-sodium has been shown to be stable under these conditions, the inorganic lead must have come from the decomposition of diethylallyllead-sodium. If this is true, the sum of the per cent yields of inorganic lead and diethylallylmethyllead gave the per cent of material from which an ethyl group was cleaved (12.7%). The yield of triethylmethyllead signified the per cent of triethylallyllead from which an allyl group was cleaved (63%). Therefore, the ratio of the numbers of allyl to ethyl groups cleaved was 63:13 (14:3); whereas, if no preference was shown, the ratio would have been 1:3. Therefore, a strong preference for cleaving the allyl group was shown.

Triethylbenzyllead

Cleavage by sodium

An ether solution of 38.5 g. (0.1 mole) of triethylbenzyllead was cleaved by 4.6 g. (0.2 g. atom) of sodium, as described in the general method. The reaction mixture developed

a red color during the cleavage, but the color changed to a yellow when the 19 g. (0.2 mole) of methyl bromide was added. A second run was made on 35.4 g. (0.0925 mole) of triethylbenzyllead, and proportional amounts of the other chemicals were used. The amount of lead chromate isolated was 4.8 g. (15%) in the first run and 2.85 g. (9.5%) in the second. The yields of organolead compounds were as follows: triethylmethyllead, 20.4 g. (66%) and 17.4 g. (61%); a liquid boiling at 132-140° (10 mm.), 2.6 g. and 4.4 g. The observed physical constants for triethylmethyllead were b.p. 69° (15 mm.), n_D^{23} 1.5160, and d_4^{23} 1.7133.

The high-boiling material could not be separated by fractional distillation; so it was cleaved with bromine and treated with ethylmagnesium bromide according to the method of Gruttner and Krause (54). Fractional distillation of the resulting organolead compounds gave a product which distilled at 87-88° (24 mm.). This fraction had a density (d_4^{23}) of 1.7110; therefore, this fraction must be triethylmethyllead. Consequently, there must have been some diethylbenzylmethyllead in the high-boiling fraction.

In the second run, the reaction mixture was distilled with steam just after hydrolysis. The distillate was dried and subjected to fractional distillation, and the toluene fraction was nitrated. The yield of 2,4-dinitrotoluene (m.p. 69-70°) was 1.8 g. (11%). A mixed melting point was

not depressed.

Sixty-three per cent of the triethylbenzyllead underwent cleavage of a benzyl group and not more than 22% of the organolead compound underwent cleavage of an ethyl group. The 22% was a maximum, since it was the sum of the yields of inorganic lead and high boiling fraction. The ratio of the benzyl to ethyl groups cleaved was 63:22 (8.6:3), but the ratio of benzyl to ethyl groups in the starting material was 1:3; therefore, a strong preference for the cleavage of the benzyl group was shown.

Triethyl-s-butyllead

Cleavage by sodium

The general method was applied to cleave 35.1 g. (0.1 mole) of triethyl-s-butyllead with 4.6 g. (0.2 g. atom) of sodium. Again, 19 g. (0.2 mole) of methyl bromide was used for derivatization. The reaction was worked up in the usual way to yield 14.6 g. (47.5%) of triethylmethyllead and 11.8 g. (35%) of a fraction boiling at 102° (17 mm.). The triethylmethyllead was identified by the constants b.p. 71° (16 mm.), n_D^{24} 1.5153, and d_4^{23} 1.7110.

The high-boiling fraction was refractionated; and the middle portion, boiling steadily at 87.5° (10 mm.), was separated and gave a refractive index (n_D^{20}) of 1.5180 and a

density (d_4^{20}) of 1.5892. Also, a lead analysis checked the theoretical value for diethyl-s-butylmethyllead.

Anal. Calcd. for $C_9H_{22}Pb$: Pb, 61.4. Found: Pb, 61.7 and 61.3.

The ratio of the ethyl to s-butyl groups cleaved was 35:47.5 or 3:4, but the ratio of the number of them in the starting material was 3:1; therefore, the s-butyl group was cleaved more readily than the ethyl group.

Identification of diethyl-s-butylmethyllead

Five grams of diethylmethylphenyllead was dissolved in 25 cc. of dry ether, and solid carbon dioxide was added until an excess was present. A solution of bromine in ether was added slowly until the bromine color remained one minute. The excess carbon dioxide was expelled, and the ether solution dried (54) before it was poured into an ether solution containing an excess of s-butylmagnesium bromide. The reaction was refluxed for 15 minutes, then poured on iced-ammonium chloride and worked up in the usual way. The main product was 2 g. (43%) of an oil, diethyl-s-butylmethyllead, with the following physical constants: b.p. 76-78° (16 mm.), n_D^{20} 1.5167, and d_4^{20} 1.5880.

Triethylmethyllead

Cleavage by sodium

A solution of 30.9 g. (0.1 mole) of triethylmethyllead in ether was added to a solution of 4.6 g. (0.2 g. atom) of sodium in liquid ammonia. This reaction was run and worked up as described above in the general method. However, 24.6 g. (0.2 mole) of n-propyl bromide was the alkyl halide that was added to derivatize the cleavage products. Upon fractionation, two products were obtained. One of the products was diethylmethyl-n-propyllead and amounted to 27.4 g. (85%). The observed constants for this product were b.p. 76° (11 mm.), n_D^{22} 1.5138, and d_4^{22} 1.6408. These values check satisfactorily with the following reported values: b.p. 80.5 (15 mm.), $n_D^{22.1}$ 1.5141, and $d_4^{22.1}$ 1.6403 (54). The second product obtained was 0.5 g. of a compound which boiled at 84-86° (11 mm.) and had a refractive index (n_D^{20}) of 1.5153. These values indicated that this compound was probably mostly triethyl-n-propyllead, but it was produced in no more than 1.5% yield. The constants that have been reported for triethyl-n-propyllead are b.p. 99.5° (16 mm.) and $n_D^{19.7}$ 1.5175 (57).

The ratio of ethyl to methyl groups cleaved was 85:1.5 or 57:1, but the ratio of the number of them in the starting material was 3:1; therefore, the ethyl group was cleaved

preferentially.

Triethylphenyllead

Cleavage by lithium

The cleavage was run as described in the general method, but only one-half of the amounts of chemicals were used. Lithium was used as the cleaving agent. Thus, 18.6 g. (0.05 mole) of triethylphenyllead in ether was added to a solution of 0.69 g. (0.1 g. atom) of lithium in liquid ammonia. For derivatization, 9.5 g. (0.1 mole) of methyl bromide was added. The only organolead compound that could be isolated was diethylmethylphenyllead, but it was produced in an 86% (15.2 g.) yield. The physical constants were b.p. 132° (15 mm.) and d_4^{20} 1.7025.

The cleavage was repeated under the same conditions but with double the quantity of reagents mentioned above. The product boiled at 131° (15 mm.) and 98° (4 mm.). The yield of diethylmethylphenyllead from this run was 32.8 g. (90%). An analysis of this compound checked the theoretical value.

Anal. Calcd. for $C_{11}H_{12}Pb$: Pb, 58.01. Found: Pb, 57.97 and 57.92.

The ethyl group was cleaved exclusively from triethylphenyllead.

Identification of diethylmethylphenyllead

The properties of diethylmethylphenyllead have not been reported. Consequently, to establish the identity of this product, the phenyl group was replaced by a bromine; and the bromine was replaced by an n-propyl group to yield the known diethylmethyl-n-propyllead. A solution of 16.3 g. (0.046 mole) of diethylmethylphenyllead in 80 cc. of ether was cooled by the addition of solid carbon dioxide, and then a solution of 7.5 g. of bromine in 10 cc. of ether was added until the bromine color remained for one minute (54). The reaction was allowed to warm up, and was then refluxed for five minutes. The ether solution was dried by means of sodium sulfate and was added to an excess of a solution of n-propylmagnesium bromide. After the mixture was refluxed for 15 minutes, the solution was poured on iced-ammonium chloride and worked up in the usual way. The main fraction boiled at 84-85° (17 mm.), and after refractionation gave a yield of 5.9 g. (40%). The properties of this product were b.p. 84-85° (17 mm.), n_D^{22} 1.5155, and d_4^{22} 1.6300. These properties check satisfactorily with those reported for diethylmethyl-n-propyllead; therefore, the product from the above cleavage was diethylmethylphenyllead. The reported constants for diethylmethyl-n-propyllead are b.p. 80.5° (15 mm.), $n_D^{22.1}$ 1.5141, and d_4^{22} 1.6403 (54).

Trimethylphenyllead

Cleavage by sodium

A solution of 4.6 g. (0.2 g. atom) of sodium in liquid ammonia was used to cleave 32.9 g. (0.1 mole) of trimethylphenyllead according to the general method previously described. The organolead-sodium compounds were derivatized by the addition of 24.6 g. (0.2 mole) of n-propyl bromide. When the mixture was worked up, only dimethylphenyl-n-propyllead could be found, but it was isolated in an 31.4 g. (88%) yield. The physical constants for the products were b.p. 93° (3 mm.), n_D^{20} 1.5713, and d_4^{24} 1.6932. A lead analysis was also run on the product.

Anal. Calcd. for $C_{11}H_{18}Pb$: Pb, 58.02. Found: Pb, 57.92 and 57.90.

This cleavage was repeated, but only one-third of the quantities of reagents mentioned above were used. In this run, 10 g. (76%) of dimethylphenyl-n-propyllead was obtained. The physical characteristics were b.p. 95° (4 mm.) and n_D^{20} 1.5718.

The results of these two experiments showed that the methyl group was the only one cleaved.

Triphenyl-p-dimethylaminophenyllead

Cleavage by sodium

A mixture of 17 g. (0.03 mole) of triphenyl-p-dimethylaminophenyllead, 42 cc. of ether and 60 cc. of liquid ammonia was cooled to -70° in a nitrogen atmosphere, and 1.38 g. (0.06 g. atom) of sodium was added. Even after thirty minutes of reaction, the sodium color still persisted; so the cooling bath was removed. After an additional forty-five minutes, the color of the sodium had disappeared and was replaced by a light green color. An excess, 32.7 g. (0.3 mole), of ethyl bromide in 35 cc. of ether was added, and the mixture was allowed to stir until the ammonia evaporated. The volatile solvents were distilled off and the mixture was distilled with steam. All of the distillate was collected together and extracted with dilute hydrochloric acid. The ether solution was fractionated to separate the ether and benzene. The benzene was forced over after the addition of di-n-butyl ether and further fractional distillation. All fractions which may have contained benzene were treated with cold concentrated sulfuric acid, and the sulfuric acid was extracted with purified petroleum ether. The petroleum ether solution was nitrated (68) to give 0.65 g. (13%) (0.0039 mole)

(68) See ref. 53, p. 138.

of m-dinitrobenzene (m.p. 85-87°). Recrystallization gave pure m-dinitrobenzene as evidenced by the fact that an authentic sample did not depress the mixed melting point. The benzene was not recovered by a very efficient method; so the efficiency was checked by a control separation and nitration.

A solution of 2 cc. (0.0225 mole) of benzene in 95 cc. of ether was distilled through the same column as had been used above with the same precautions and treated in the same way. After nitration, 0.98 g. of m-dinitrobenzene (m.p. 87-89°) was obtained. In the control, the isolation of 0.98 g. of m-dinitrobenzene meant that 0.0225 mole of benzene was present at the start of the separation of the products. By a direct proportion, the isolation of 0.65 g. of m-dinitrobenzene meant that 0.015 mole of benzene was formed in the cleavage reaction described above. This 0.015 mole represented a 50% yield of benzene.

The hydrochloric acid extract was made strongly basic with sodium hydroxide, saturated with sodium chloride and extracted with ether. The ether extract of amines was evaporated, and the residue was treated twice with benzenesulfonyl chloride and sodium hydroxide solution (69). The dimethylaniline was extracted from the basic solution by means of ether. The ether solution was dried, and the ether was distilled off. The

(69) See ref. 53, p. 25.

picrate of the residue was then made according to the directions by Shriner and Fuson (70). The 0.4 g. of yellow precipitate melted at 155-159°, but two recrystallizations raised the melting point to 162-163°. A mixed melting point with a sample of dimethylaniline picrate was not depressed.

A sample of 0.15 cc. (0.0012 mole) of dimethylaniline was treated in exactly the same way and yielded 0.41 g. of crude picrate (m.p. 159-160°). In this case, 0.41 g. of picrate represented the presence of 0.0012 mole of dimethylaniline; therefore, the 0.4 g. of picrate from the cleavage product meant that 0.0012 mole (4%) of dimethylaniline was produced from the cleavage.

The cleavage was repeated under the same conditions with 12 g. (0.0215 mole) of triphenyl-p-dimethylaminophenyllead and corresponding amounts of the other chemicals. The products obtained were 0.37 g. of m-dinitrobenzene and 0.74 g. of dimethylaniline picrate. These yields represented a production of 39% benzene and 10% dimethylaniline. The mixture of organolead compounds could not be separated.

The average yields from these runs show that the ratio of the number of phenyl to p-dimethylaminophenyl groups cleaved was 45:7 or 6.4:1. The ratio of the number of groups in the starting material was 3:1. A preference for a cleavage of the phenyl group was shown.

(70) See ref. 53, p. 140.

DISCUSSION

Preparation of Organolead-sodium Compounds

As pointed out previously in this thesis, there was only one report of an organic group being cleaved from an organolead compound by a reactive metal. This report was that a triphenylmethyl group was cleaved from triphenyltriphenylmethyllead by sodium. The C-Pb bond that was broken in this case was an uncommonly weak one; therefore, one could not justifiably predict that organolead compounds in general would be cleaved by sodium. Evidence of the weakness of this bond was found in the report that triphenyltriphenylmethyllead dissociated spontaneously into triphenylmethyl and triphenyllead (23).

From the results of several reports, it may be seen that the order of increasing ease of cleavage of certain C-M bonds is C-Si < C-Ge < C-Sn. If this order may be extended one step more, C-Pb bonds should be cleaved even more readily than C-Sn bonds. The experiments described in this thesis have shown that the cleavage of organic groups from organolead compounds is a general reaction, since p-dimethylaminophenyl, phenyl, methyl, ethyl, n-butyl, s-butyl, allyl, and benzyl groups were all shown to be cleaved from appropriate organolead compounds.

This cleavage reaction is an important method for the preparation of organolead-sodium compounds, as may be seen when this method is compared with the two other important methods which have been reported. The other two methods are, first, the reaction of triorganolead halides with sodium in liquid ammonia, and second, the reaction of hexaorganodilead compounds with sodium in liquid ammonia.

From the standpoint of the yield of triphenyllead-sodium, based on the amount of tetraphenyllead used, the best method was the direct cleavage of tetraphenyllead with sodium in liquid ammonia which gave an eighty-three per cent yield. When the tetraphenyllead was first treated with iodine to yield triphenyllead iodide, then the iodide treated with sodium in liquid ammonia, the yield of triphenyllead-sodium was seventy-nine per cent (25). The yield of triphenyllead-sodium would be slightly lower, due to manipulation losses, when one employs the addition of sodium to hexaphenyldilead. However, an extra step, isolation of the hexaphenyldilead, is involved. If triphenyllead chloride was chosen as an intermediate triorganolead halide the over-all yield of triphenyllead-sodium was sixty-eight per cent. Therefore, the direct cleavage method gives the highest yield of triphenyllead-sodium.

The yields of trialkyllead-sodium compounds from these three methods are probably very much alike. A definite figure for the yield of triethyllead-sodium from the reaction of

sodium with either triethyllead chloride or hexaethyldilead cannot be given, but the yield in either case cannot be appreciably higher than that obtained by the direct cleavage of tetraethyllead with sodium. The yield in the latter case was ninety-five per cent.

From the standpoint of the availability of the starting materials, the direct cleavage method for the preparation of organolead-sodium compounds has a distinct advantage. In almost every case, symmetrical organolead compounds are more readily available than organolead halides or hexaorganodilead compounds.

When purity is the factor of prime importance, it is advisable to prepare triphenyllead-sodium from hexaphenyldilead. Triphenyllead chloride and sodium gave practically a quantitative yield of triphenyllead-sodium, but a small amount of dark solid also formed. The production of this solid showed that an impurity was formed. The constitution of this impurity is not known. Cleavage of tetraphenyllead with sodium gave sodamide as a by-product; however, the sodamide may be removed. Two methods are available for the removal of sodamide; first, the solution of triphenyllead-sodium may be filtered through a sintered glass plate, and second, an equivalent of ammonium bromide may be added. The ammonium bromide destroys the sodamide in preference to the triphenyllead-sodium; however, one must avoid adding an excess of

ammonium bromide. All of these methods yield solutions of triphenyllead-sodium which are pure enough for most purposes. However, if sodamide is not removed at least two equivalents of benzyl chloride must be added for derivatization.

Since hexaethyldilead reacts with air and is of limited stability, the most pure solutions of triethyllead-sodium are probably best prepared by the reaction of either triethyllead chloride or tetraethyllead with sodium followed by filtration. The addition of ammonium bromide cannot be used as a method to destroy sodamide in the presence of triethyllead-sodium, since the latter compound also reacts vigorously with ammonium bromide. Thus, ammonium bromide destroys some of both compounds.

Obviously, the direct cleavage of organolead compounds with sodium, being a one-step process, requires much less time than any of the other methods. Both of the other methods require the isolation of at least one intermediate compound, either an organolead halide or a hexaorganodilead compound.

From these comparisons, it may be stated that the preparation of organolead-sodium compounds by the direct cleavage of symmetrical organolead compounds has many advantages over other methods of preparation, and it has no serious disadvantages.

In some preliminary work, an attempt was made to cleave the ethyl or n-butyl group preferentially from triethyl-n-butyllead by means of sodium; then the organolead-sodium

compounds were derivatized by the addition of methyl bromide. From the yields of diethyl-n-butylmethyllead and triethylmethyllead obtained, it could be seen that the n-butyl group was cleaved slightly more easily than the ethyl group. It was believed that the difference between the ease of cleavage of the groups should be greater than was shown; and that if the reaction could be slowed down, a more pronounced difference would be seen. Several experiments were run under different conditions to try to slow down the cleavage of tetraphenyl- and tetraethyllead and still obtain a good yield of organo-lead-metal compounds. Some general facts which have been observed in connection with these studies may be mentioned.

The cleavage of tetraphenyllead was very rapid. It was essentially complete in one minute but should be allowed at least six minutes to use up as much of the tetraphenyllead as possible. The rate was about the same whether the reaction was run in liquid ammonia alone or in ether-liquid ammonia mixed solvent.

The rate of cleavage of tetraethyllead was more dependent upon the solvent. In liquid ammonia alone, the cleavage required fourteen minutes. In toluene-ammonia mixed solvent, the cleavage required three minutes. In ether-ammonia mixed solvent, the blue color of the sodium faded as rapidly as the tetraethyllead was added.

Cooling the reaction to -70° greatly increased the time

of cleavage of tetraphenyllead, but did not increase the time of cleavage of tetraethyllead nearly as much. There was a greater difference between the rates of cleavage of an ethyl-Pb bond and a phenyl-Pb bond at lower temperatures; therefore, preferential cleavage studies should be run at low temperature.

Higher yields of triethyllead-sodium and triphenyllead-sodium were obtained when ether-liquid ammonia mixed solvent rather than liquid ammonia alone was used as a cleavage medium. Toluene-liquid ammonia solvent is better than liquid ammonia alone but not so good as ether-liquid ammonia.

Tetraphenyllead gave higher yields of triphenyllead-sodium when the cleavage was run in more dilute solutions (100 equivalents of ether and 270 equivalents of liquid ammonia) than when it was run in more concentrated solutions (20 equivalents of ether and 73 equivalents of liquid ammonia).

A comparison of the ability of various metals to cleave tetraphenyllead was made, the results of which are shown in Table I (p. 53). The ability to cleave was judged by the yield of triphenylbenzyllead found after the cleavage was allowed to continue for a definite period, and the triphenyllead-sodium was derivatized by the addition of benzyl chloride. The metals placed in order of cleaving ability are K, Na > Li, Ca, Sr > Ba. Magnesium did not dissolve in liquid ammonia to an extent sufficient to cleave tetraphenyllead. Calcium, lithium, and sodium showed very little difference in ability

to cleave tetraethyllead, for upon derivatization of the cleavage products with n-butyl bromide, the yields of triethyl-n-butyllead agreed very closely in the three cases.

The order of addition of the ether, tetraethyllead, liquid ammonia, and sodium had no pronounced effect on the time of cleavage or yield of product.

A reasonable excess of sodium may be used in the preparation of either triphenyllead-sodium or triethyllead-sodium. The reaction does not easily continue with the removal of one more organic group to yield diphenyllead-disodium or diethyllead-disodium. When tetraphenyllead was allowed to react with a large excess of sodium (over eight equivalents) for two and three-quarters hours, there was a slight decrease in the yield of triphenyllead-sodium, but no evidence for the formation of diphenyllead-disodium was found. The reaction mixture was not red and did not produce diethyldiphenyllead when ethyl bromide was added. These two properties are characteristic of diphenyllead-disodium (28).

It has been definitely proved that two ethyl groups could be cleaved from tetraethyllead and under much more mild conditions than were used for tetraphenyllead. Proof that two ethyl groups were removed lies in the fact that derivatization with methyl bromide led to the formation of diethyldimethyllead. However, even in this case, the second ethyl group was cleaved with considerably more difficulty than the first; so there

would be no more than a trace of R_2PbNa_2 compounds formed during the preparation of R_3PbNa compounds if reasonable care is exercised.

As mentioned earlier in this report, Chambers and Scherer (21) claimed that it was easier to cleave a phenyl group from triphenyltin-sodium than it was to cleave a methyl group from trimethyltin-sodium. It was also pointed out in this thesis that they lacked sufficient evidence for such a statement. Due to the similarity of the methyl and ethyl groups, it may be predicted that the opposite would be true of organolead compounds, since the ethyl group was cleaved from triethyllead-sodium more readily than the phenyl group was cleaved from triphenyllead-sodium.

When tetraphenyllead was allowed to react with a large excess of sodium for several hours, the yield of triphenyllead-sodium slowly decreased. This decrease may have been due to the cleavage of a phenyl group from the triphenyllead-sodium, but if this was true, the diphenyllead-disodium that was produced was unstable under these conditions. However, diethyllead-disodium was stable under similar conditions. A comparison of these results hint that it may be more wise to work with diethyllead-disodium rather than diphenyllead-disodium in studies on the preparation and properties of $R_2PbM'_2$ compounds.

This thesis reports the preparation of the first

unsymmetrical organolead-sodium compounds. They react normally and are relatively stable; however, diethylbenzyllead-sodium and diethylallyllead-sodium seemed to undergo some decomposition even at -70°.

Several attempts were made to cleave organolead compounds in inert solvents, and thus obtain solutions of organolead-sodium compounds that were free of ammonia. Mild conditions must be used, or cleavage will be complete with the formation of free lead. When sodium was allowed to react with organolead compounds in ether, the bright surface of the sodium gradually darkened until it became quite black; then the reaction seemed to stop. The darkening may have been due to deposition of either organosodium compounds or free lead. It probably was not the former since organosodium compounds, particularly ethylsodium, are destroyed rapidly by ether. Apparently a coating of lead on the sodium stopped the reaction.

An attempt was made to cleave triphenylbenzyllead by sodium amalgam in ether. The amalgam was used to avoid the formation of a coating on the sodium. However, the triphenylbenzyllead was not cleaved.

The binary mixture ($Mg + MgI_2$), acting as if it were a solution of magnesious iodide, has reactions similar to those of a metal (71). An attempt was made to cleave

(71) Gomberg and Bachmann, J. Am. Chem. Soc., 49, 236 (1927); 52, 2455 (1930). See also, ref. 58, p. 69.

triphenylbenzyllead by means of the binary mixture. There was no evidence of reaction, for none of the magnesium seemed to have been dissolved. Slowly the solution changed color, and when the mixture was worked up, the products were found to be tetraphenyllead, triphenylbenzyllead and an unstable organo-lead compound. Apparently, a redistribution reaction took place slowly. There are no reports that either magnesium iodide or magnesious iodide causes a redistribution reaction, but it is reasonable to assume it does since many metal halides do (72). A redistribution reaction of triphenylbenzyllead should have also produced dibenzyldiphenyllead, tribenzyl-phenyllead and tetrabenzyllead. However, a lead compound which contains two or more benzyl groups is unstable and decomposes when heated (73). This fact accounts for the decomposition that took place when the reaction was worked up.

Tetraethyllead, in an ether solution, was not cleaved noticeably by sodium, although the surface of the metal turned dark. When ammonia gas was introduced, a reaction took place with the evolution of heat. The solution turned yellow, a color which is characteristic of triethyllead-sodium; then a red color developed. The production of a red color meant that

(72) Calingaert and co-workers, ibid., 61, 2748, 2755, 2758, 3300 (1939); 62, 1099, 1104, 1542, 1545 (1940); 63, 947 (1941).
(73) Krause and Schlöttig, Ber., 63, 1381 (1930).

triethyllead-sodium was being destroyed, probably by further cleavage to yield diethyllead-disodium. Apparently, it was more difficult to stop the reaction at the first stage in ether than it was in liquid ammonia. Triphenyllead-sodium forms a complex with ammonia (27), and the formation of a complex often makes a compound more stable and less reactive. Hence, it is possible that ammonia stabilized the triethyllead-sodium toward further cleavage long enough for it to escape from the surface of the sodium. In this way, the tetraethyllead would not be immediately cleaved to free lead, and the free lead could not coat the surface of the sodium.

Neither dimethylaniline nor triethylamine were capable of preventing the formation of a black coat on the sodium. It may be that trimethylamine could take the place of ammonia gas in promoting this cleavage reaction in inert solvents.

Reaction of Organolead-sodium Compounds with Organic Halides

The organic group of the organolead-sodium compound had pronounced influence on the extent with which these compounds reacted with organic halides. The organic groups which were present in particularly stable hexaorganodilead compounds were also present in the organolead-sodium compounds that reacted less completely with benzyl chloride. For example, both hexa-o-anisyldilead and hexacyclohexyldilead were quite

stable, and benzyl chloride reacted incompletely with both tri-o-anisyllead-sodium and tricyclohexyllead-sodium (25). This incomplete derivatization may be explained, at least in the former case, as being due to a steric hindrance caused by the methoxy groups in the ortho positions.

Several observations have indicated that triethyllead-sodium was more reactive than triphenyllead-sodium. First, triethyllead-sodium, mixed with an equal amount of sodamide, was derivatized completely by the addition of one and one-half equivalents of n-butyl bromide. This observation meant that triethyllead-sodium was more reactive than sodamide toward n-butyl bromide. However, triphenyllead-sodium, mixed with an equal amount of sodamide, was not derivatized at all by the addition of one and seven-tenths equivalents of ethyl bromide. Triphenyllead-sodium did not react with alkyl halides unless quite an excess of the halide was present, but triethyllead-sodium did react with these halides completely if only a small excess of the halide was present. Therefore, triethyllead-sodium was more reactive than triphenyllead-sodium.

Second, when ammonium bromide was added to a mixture of sodamide and triphenyllead-sodium, the sodamide was completely destroyed before any of the triphenyllead-sodium was destroyed. This was another indication that sodamide was more reactive than triphenyllead-sodium. However, when ammonium bromide was added to a mixture of sodamide and triethyllead-sodium, about

thirty per cent of the triethyllead-sodium was destroyed. From these results, it was concluded that sodamide and triethyllead-sodium were of about the same reactivity toward ammonium bromide. Therefore, triethyllead-sodium was more reactive than triphenyllead-sodium.

Third, triethyllead-sodium reacted with bromobenzene to give a seventy-seven per cent yield of triethylphenyllead, but triphenyllead-sodium either did not react with p-bromotoluene or gave a very poor yield of triphenyl-p-tolyllead. Trimethyllead-sodium reacted with bromobenzene to give a forty-two per cent yield of trimethylphenyllead. These three results indicated that the order of decreasing reactivity was as follows: triethyllead-sodium > trimethyllead-sodium > triphenyllead-sodium.

Two different organic groups may be present at the same time in the organolead-sodium compound; for example in the compounds diethylallyllead-sodium, diethylbenzyllead-sodium, diethyl-s-butyllead-sodium, diethyl-n-butyllead-sodium, diethylmethyllead-sodium, diethylphenyllead-sodium and dimethylphenyllead-sodium. These compounds reacted normally with alkyl halides; however, the benzyl and allyl derivatives appeared to be unstable since some decomposition seemed to take place even at -70°.

Tetraphenyllead was cleaved with various metals, and then derivatized with benzyl chloride, in order to determine

which metal was most effective in the production of a high yield of triphenylbenzyllead. The metals arranged in decreasing order of effectiveness are as follows: Na, K > Sr, Ca, Li > Ba. Sodium, calcium and lithium, were of equal effectiveness in the production of a high yield of triethyl-n-butyllead by derivatization of the cleavage product of tetraethyllead by metals.

The extent of coupling of an organic halide with an organolead-sodium compound was markedly influenced by the type of organic group in the organic halide. The least reactive ones tried were the aryl halides. Triphenyllead-sodium did not couple to an appreciable extent with any of the following aryl halides: p-chlorotoluene, p-bromotoluene, p-iodotoluene, methyl p-bromobenzoate, p-iodonitrobenzene, and 2,4-dinitrochlorobenzene. However, triethyllead-sodium did couple with the phenyl group of bromobenzene to give satisfactory yields of triethylphenyllead.

Ethyl bromide, a typical alkyl halide, coupled with triphenyllead-sodium to give a satisfactory yield of triphenylethyllead only if a large excess of the ethyl bromide was added. However, only a small excess of an alkyl halide was necessary to derivatize completely triethyllead-sodium. Methyl bromide, ethyl bromide, n-propyl bromide, and n-butyl bromide are the alkyl halides that have been shown to undergo the coupling reaction with triethyllead-sodium almost quantitatively.

It was interesting to notice the influence of a branched aliphatic chain on the speed and completeness of derivatization of triethyllead-sodium. The derivatization was almost instantaneous and practically quantitative when n-butyl bromide was added. The derivatization was noticeably slower and thirteen per cent less complete when s-butyl bromide was added. The derivatization did not take place at all when t-butyl bromide was added. There were probably three factors which prevented t-butyl bromide from coupling with triethyllead-sodium: first, steric hindrance would be a factor in holding the t-butyl group away from the triethyllead group; second, t-butyl bromide is less reactive than the other alkyl halides that were used (74); and third, t-butyl bromide undergoes dehydrohalogenation more readily than the other halides mentioned, and the hydrogen bromide formed would destroy the triethyllead-sodium.

The more reactive halide, benzyl chloride, derivatized the triphenyllead-sodium completely to produce triphenylbenzyllead, even though only a slight excess of the halide was added. Likewise, allyl chloride, which is similar to benzyl chloride in reactivity, derivatized triethyllead-sodium to give a high yield of triethylallyllead. In contrast to this last reaction, benzyl chloride reacted with triethyllead-sodium to give a

(74) See ref. 36, pp. 842, 844.

poor yield of triethylbenzyllead. When the two compounds were mixed, a vigorous reaction took place, and the liquid organolead product was stable until heated up to the boiling point of triethylbenzyllead; then decomposition took place. When benzyl chloride was added to the liquid ammonia solutions which contained sodamide, stilbene was produced. However, stilbene could be formed only by the dehydrohalogenation of benzyl chloride. Since sodamide can cause a dehydrohalogenation of benzyl chloride, it may be that triethyllead-sodium, being of similar reactivity, could also remove hydrogen chloride from benzyl chloride. The formation of hydrogen chloride would lead to the destruction of the triethyllead-sodium. This reasoning provides a possible explanation for the production of only a poor yield of triethylbenzyllead from the reaction of triethyllead-sodium with benzyl chloride.

The reaction of only one dihalide, ethylene dibromide, was tried with organolead-sodium compounds. Triphenyllead-sodium did not couple with ethylene dibromide to produce triphenyl-β-bromoethyllead even when the solution of the former compound was slowly added to an excess of ethylene dibromide. Hexaphenyldilead was the main product. Advantage was taken of this observation to develop a convenient, rapid method for the preparation of hexaphenyldilead. The yield of hexaphenyldilead was fifty-eight per cent. This yield was thirteen to twenty-five per cent less than the yields obtained

by the conversion of tetraphenyllead to the chloride or iodide, followed by the addition of a liquid ammonia solution of sodium (25), but the preparation by the reaction of triphenyllead-sodium and ethylene dibromide was much more rapid.

The reactivity of the halogen of the organic halide had a pronounced influence on the completeness of the coupling reaction. The reactivity of the halogen is intimately associated with the nature of the organic group of the organic halide, and since the influence of the organic group has already been discussed (p. 122), reference may be made to that section to review the influence of the reactivity of the halogen on the completeness of the reaction. However, two additional cases may be mentioned. A small yield of triphenyl-p-tolyllead was obtained by the reaction of triphenyllead-sodium with p-iodotoluene, but no triphenyl-p-tolyllead could be isolated after triphenyllead-sodium was mixed with either p-bromotoluene or p-chlorotoluene. We are therefore led to the conclusion that aryl iodides have more of a tendency than aryl bromides or chlorides to couple with triphenyllead-sodium.

This observation cannot be carried over to the reactions of triethyllead-sodium. Bromobenzene rather than iodobenzene gave the higher yield of triethylphenyllead when the aryl halides were allowed to react with triethyllead-sodium. In the case of iodobenzene, there seemed to be a side reaction which used up the triethyllead-sodium before it had a chance

to couple with that aryl halide.

Salts, such as sodium p-iodobenzoate, did not react with triethyllead-sodium, possibly due to the insolubility of the salt in the reaction medium (63). An ester, ethyl p-bromobenzoate, underwent ammonolysis before it reacted with triphenyllead-sodium. Aromatic nitro compounds react with liquid ammonia to form compounds which apparently destroy the triphenyllead-sodium.

From these observations several recommendations may be made as guides in further work. First, avoid organic groups which offer steric hindrance. This applies for the organic groups in both the triorganolead-sodium compound and the organic halide. Second, avoid the use of triaryllead-sodium compounds with the lesser reactive halides. Third, use a large excess of an alkyl halide to obtain a satisfactory yield of a triarylalkyllead from a triaryllead-sodium compound. Fourth, successful coupling is more apt to be obtained by the use of trialkyllead-sodium compounds than with triaryllead-sodium compounds unless the organic halide undergoes dehydrohalogenation easily. Fifth, it is more advisable to use sodium than other reactive metals. Sixth, the use of t-alkyl halides should be avoided. Since these recommendations were made on a limited number of observations, it must not be expected that they will be valid in every case.

Preferential Cleavage of Organolead Compounds

It would be convenient if a study of the ease of cleavage of groups from organolead molecules could be based on the time required for the organolead compound to use up two equivalents of sodium, but this method was shown to give contradictory results. When liquid ammonia alone was used as a solvent, in which neither organolead compound is noticeably soluble, tetraphenyllead was cleaved in four minutes, and tetraethyllead was cleaved in fourteen minutes. From these results, one would be led to say that the phenyl group was cleaved more readily than the ethyl group. When ether-liquid ammonia mixed solvent was used, in which tetraethyllead was completely soluble and tetraphenyllead only slightly soluble, tetraphenyllead was cleaved in three minutes, and tetraethyllead was cleaved instantaneously. From these results, one would be led to the opposite conclusion, that the phenyl group was cleaved less readily than the ethyl group. This difficulty may be due to differences in solubility, but no inert solvent was found which would dissolve an appreciable amount of both tetraethyllead and tetraphenyllead at the temperature of liquid ammonia.

The most direct comparison on the ease of cleavage of groups was to attach both groups to the same lead atom, then to cleave the resulting unsymmetrical organolead compound with sodium. The organolead-sodium compounds that were formed could

not be isolated; so they were derivatized by the addition of an appropriate alkyl halide. By the ratio of the amounts of the various products formed, one could determine the amounts of each of the original groups cleaved, or the relative ease of cleavage of each group.

In order to select the best metal to use for the study of the preferential cleavage of an unsymmetrical organolead compound, the cleavages of triethyl-n-butyllead by lithium, by sodium, and by calcium were compared. The cleavage products were derivatized by the addition of methyl bromide, and the products were separated. The results are collected in Table II.

Table II

Metal	% yield of $(C_2H_5)_3PbCH_3$	% yield of $(C_2H_5)_2(n\text{-}C_4H_9)PbCH_3$	Ratio of groups cleaved C_2H_5:n-C_4H_9
Ca	15	44.5	3:1
Li	21	59	3:1.1
Na	26	54.5	3:1.4

The amount of triethyl-n-butyllead from which an ethyl group was cleaved was determined by the yield of diethyl-n-butyl methyllead, and the amount of starting material from which an n-butyl group was cleaved was determined by the yield of triethylmethyllead. The ratio of the ethyl to n-butyl groups cleaved would be the ratio of the yield of diethyl-n-butylmethyllead to the yield of triethylmethyllead.

If the cleaving metal showed no preference for either group, the ratio of ethyl to n-butyl groups cleaved would be 3:1. The results in Table II indicate that the cleaving metals showed very little preference for one group over the other; but when a preference was shown, the n-butyl group was slightly easier to cleave than the ethyl group.

The cleavage of several other unsymmetrical organolead compounds by sodium was carried out. The ratios of the groups cleaved from each unsymmetrical organolead compound tested are shown in Table III.

Table III

Compound tested	Ratio of groups cleaved
triethylallyllead	ethyl : allyl = 3:14
triethylbenzyllead	ethyl : benzyl = 3:8.6
triethyl-s-butyllead	ethyl : s-butyl = 3:4
triethyl-n-butyllead	ethyl : n-butyl = 3:1.4
triethylmethyllead	ethyl : methyl = 57:1
triphenyl-p-dimethyl-aminophenyllead	phenyl : p-dimethylamino-phenyl = 6.4:1
triethylphenyllead	ethyl : phenyl = 88:0 (75)
trimethylphenyllead	methyl : phenyl = 82:0 (75)

(75) The ratios are indeterminate; so the per cents are quoted.

From the results in Table III, the series of groups arranged in order of decreasing ease of cleavage with sodium is allyl > benzyl > s-butyl > n-butyl > ethyl > methyl > phenyl > p-dimethylaminophenyl.

It is interesting to compare this order of groups with the order obtained in certain other cleavage studies. The most complete series, based on the cleavage of unsymmetrical organomercury compounds by hydrogen chloride, was presented by Kharasch and co-workers (76), but this thesis is concerned with only a few of the groups of Kharasch's series. These groups placed in order of decreasing ease of cleavage from organomercury compounds by hydrogen chloride are phenyl > methyl > ethyl > n-butyl > benzyl (76a).

The same series was found to represent the ease of cleavage of groups from unsymmetrical organolead compounds when hydrogen halides were used as cleaving agents (23, 77). In addition, Austin (78) found that the p-dimethylaminophenyl

(76) (a) Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1932). This publication contains references to the earlier work and correlates the results of all of the published experiments. (b) Kharasch, Pines and Levine, J. Org. Chem., 3, 347 (1938); (c) Kharasch and Swartz, ibid., 3, 405 (1938); (d) Kharasch, Legault and Sprowls, ibid., 3, 409 (1938).

(77) (a) Gilman and Towne, Rec. trav. chim., 51, 1054 (1932). This publication contains references to the work done before 1932. (b) Gilman, Towne and Jones, J. Am. Chem. Soc., 55, 4689 (1933); (c) Austin, ibid., 53, 3514 (1931); 55, 2948 (1933); (d) Jones, Evans, Gulwell and Griffiths, J. Chem. Soc., 39 (1935).

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

group was cleaved more readily than the phenyl group from triphenyl-p-dimethylaminophenyllead. Again, it was Austin (77c) who published the surprising result that the allyl group was cleaved more readily than the phenyl group from triphenylallyllead. Therefore, in the cleavage of organolead compounds, both the allyl and p-dimethylaminophenyl groups are more easily cleaved from lead than any of the groups mentioned above as part of Kharasch's series.

In general, all other inorganic cleaving agents reacted with unsymmetrical organolead compounds to give the same series as was found by the cleavage with hydrogen halides. The other inorganic cleaving agents (79) that have been used are silver nitrate (80), halogens (81), thallium chloride (82), nitric acid (77d, 83), and mercuric chloride (80a, 84).

It is of interest to note that the order of cleavage of groups from organolead compounds by sodium was the reverse of the order obtained when any other inorganic cleaving agent was

(79) For a survey of cleavage reactions as well as a general review of the chemistry of organolead compounds see Calingaert, Chem. Rev., 2, 43 (1925).
(80) (a) Krause and Schlöttig, Ber., 58, 427 (1925); 63, 1381 (1930); (b) Krause and Schmitz, Ibid., 52, 2150, 2165 (1919); (c) Krause and Renwanz, Ibid., 62, 1710 (1929).
(81) Leading references to cover all of this work were collected by Kaplan, Master's thesis, Iowa State College (1939).
(82) Goddard and Goddard, J. Chem. Soc., 121, 482 (1922).
(83) Austin, J. Am. Chem. Soc., 53, 1548 (1931); Hurd and Austin, Ibid., 53, 1543 (1931).
(84) Krause and Renwanz, Ber., 60, 1582 (1927).

used, the allyl group being an exception.

The position of the allyl group in the hydrogen chloride cleavage series is surprising. Austin (77c) observed that the allyl group was cleaved first when triphenylallyllead was treated with alcoholic hydrogen bromide. Kharasch believed that the different cleaving conditions may have caused the apparent unpredicted lability of the allyl group. ThenGilman, Towne and Jones (77b) cleaved triphenylallyllead under the conditions used in other cleavage studies and found that again the allyl group was cleaved first. Since they also found that α,β-unsaturated aliphatic groups were cleaved from lead with uncommon ease, they suggested that triphenylallyllead may exist in the form $(C_6H_5)_3PbCH{=}CHCH_3$: thus the "allyl" group would no longer be expected to cleave less easily than the phenyl group.

Kharasch and Swartz then cleaved phenylallylmercury with hydrogen chloride and found the two groups cleaved at about the same rate. They assumed that the unpredicted lability of the allyl group was due to cleavage by a different mechanism, as illustrated in the following equations:

$$C_6H_5HgCH_2CH{=}CH_2 + H^+ + Cl^- \longrightarrow C_6H_5HgCH_2\overset{+}{C}HCH_3 + Cl^-$$

$$C_6H_5HgCH_2\overset{+}{C}HCH_3 + Cl^- \longrightarrow C_6H_5HgCl + CH_2{=}CHCH_3$$

This suggested mechanism may also be applied to explain why the allyl group was cleaved first from triphenylallyllead. This mechanism does not explain why both α,β- and β,γ-unsaturated groups were cleaved more readily than the phenyl group but

the γ,δ-unsaturated groups were cleaved less readily than the phenyl group. One may suggest that the addition of the proton to the C=C does not take place easily if the double bond is far (γ,δ) from the lead, but does take place with increasing ease as the position of the C=C approaches the lead atom.

The use of sodium as a cleaving agent showed the allyl group to be in its predicted position, near the benzyl group.

The most valuable series of groups (85) is the one which can be used to predict most accurately the relative reactivity of the members of a homologous series. In the majority of their reactions, the allyl and benzyl groups are very similar and are more closely related to the alkyl rather than the aryl groups. Since this would be predicted from the sodium cleavage series but not from Kharasch's series, the series obtained from the cleavage with sodium is more valuable than Kharasch's series. On the other hand, the allyl group is anomalous in some of its reactions and in its tendency to undergo rearrangements; in this sense Kharasch's series is valuable since it shows that the allyl group does act in an anomalous manner.

According to collected data on relative reactivities of homologues in several typical reactions (85), the majority

(85) A good discussion of the use of such series is given in ref. (36), p. 802.

of the reactions of benzyl compounds can be predicted more accurately from a series phenyl - ethyl - benzyl than from a series phenyl - benzyl - ethyl. Both the hydrogen chloride and the sodium cleavage give the former series, but cleavage of organolead compounds with bromine gave the latter series. Grüttner and Grüttner (60) found that the ethyl group was not cleaved in preference to the benzyl group when triethylbenzyllead was treated with bromine. This anomalous behavior was explained by the assumption that the benzyl group was oxidized off instead of being removed by direct cleavage.

When testing relative reactivities, one should use a reaction in which all compounds undergo the same reaction by the same mechanism. If one member reacts by a different mechanism, the results certainly are not comparable. It is believed that the allyl group was removed by a different mechanism than the other groups when hydrogen chloride was used as a cleaving agent. Likewise, it is believed that the benzyl group was removed by a different mechanism than the other groups when bromine was used as a cleaving agent. However, there is no evidence that any of the groups were removed by a different mechanism when sodium was used as a cleaving agent. Cleavage with sodium, then, has given more reliable results than cleavage with either hydrogen chloride or bromine.

The sodium cleavage series provides a basis for planning

the preparation of certain unsymmetrical organolead compounds. For example, in the preparation of diethyl-n-butyl-p-tolyllead, one would start with the readily available tetraethyllead, treat it with sodium, and then with p-bromotoluene. One would treat the product, triethyl-p-tolyllead, with sodium and then with n-butyl bromide. From the cleavage series one would know that the organic halides should not be used in the reverse order.

The new compounds prepared for identification purposes were diethyl-n-butylmethyllead, diethylmethylphenyllead, and diethyl-s-butylmethyllead.

In review, these studies on the preferential cleavage with sodium have given a series of groups which is almost the complete reverse of Kharasch's series. This study has also clarified the positions of the allyl and benzyl groups in the series of organic groups. This work has also provided a more convenient method for the preparation of certain unsymmetrical organolead compounds.

Suggested Mechanism of the Cleavage of Organolead Compounds by Metals

Since the series of groups placed in order of decreasing ease of cleavage by metals is the reverse of the series placed in order of decreasing ease of cleavage by other inorganic reagents, it is reasonable to suppose that these

cleavages proceed by different mechanisms.

Sodium in liquid ammonia is known to be ionized into a sodium ion and an electron (86). Since sodamide and sodium halides do not cleave organolead compounds, it cannot be the sodium ion that cleaves the organolead compounds; therefore, the electron must be the cleaving agent. The electron probably adds to the lead, temporarily increasing the number of electrons in the lead atom. This arrangement is unstable and the compound decomposes. In order to reduce the number of electrons on the lead, an organic group must break away with a pair of electrons. The lead is left with three organic groups and one unshared electron, a free radical. Such compounds react immediately with metallic sodium to give triorganolead-sodium compounds, a reaction which would take place before any more organolead compound was cleaved.

The group which broke away with the electron pair has a negative charge, and there is a positive sodium ion in solution. This mixture of charged particles is, in effect, a solution of an organosodium compound. Organosodium compounds that are stable in liquid ammonia exist in ionic form (87). Almost all of the organosodium compounds undergo ammonolysis

(86) Kraus, Chem. Rev., 8, 251 (1931).
(87) (a) Kraus and Rosen, J. Am. Chem. Soc., 47, 2739 (1925);
(b) Wooster and Mitchell, ibid., 52, 688 (1930).

immediately in liquid ammonia. This ammonolysis explains the formation of the hydrocarbon and sodamide. The equations for this mechanism are shown below.

$$Na \longrightarrow Na^{+} + \cdot^{-}$$

$$R_3PbR' + \cdot^{-} \longrightarrow [R_3\dot{P}b\bar{R}'] \longrightarrow R_3Pb + R'^{\cdot -}$$

$$R_3Pb + Na \longrightarrow R_3PbNa$$

$$R'^{\cdot -} + Na^{+} + NH_3 \longrightarrow R'H + NaNH_2$$

This mechanism is supported by the following observations:

1. The presence of the R_3PbNa compound has been proved by derivatization with $R''X$ compounds and the product (R_3PbR'') isolated and identified.

2. The production of $R'H$ has been proved by the isolation and derivatization of benzene from the cleavage of tetraphenyllead, and of toluene from the cleavage of triethylbenzyllead.

3. The presence of sodamide has been indicated by the separation of a white powder which reacts vigorously with water to give ammonia and leaves a strongly basic solution.

4. Kraus (13) mentioned that it was by no means certain that methylsodium is formed as an intermediate when tetramethyltin is cleaved by sodium in liquid ammonia. During the cleavage of triethylbenzyllead a red color appeared in the solution but the color slowly faded. The formation of a temporary red color probably meant that benzylsodium was produced because benzylsodium is known to be red in liquid

ammonia, and it slowly undergoes ammonolysis (87b, 88). A red color also formed during the cleavage of triethylallyllead, but it did not form in the cleavage of any of the other organolead compounds. The formation of a red color in these two cases only indicates that the organosodium compounds probably were formed and the ammonolysis is slow enough so a sufficient concentration of organosodium compound is formed to produce a red color.

(88) Kraus and White, ibid., 45, 777 (1923); Edelman, Linford and Burgess, Abstracts, American Chemical Society, Cincinnati (1940).

SUMMARY

A survey of the literature concerning the preparation and reactions of R_nMM' (5) compounds was made. Also, a review was made of some of the work published concerning the preferential cleavage of groups from organometallic compounds.

A study of the cleavage of organolead compounds by reactive metals was made. A number of examples showed this method to be a valuable one for the preparation of organolead-sodium compounds.

Studies were made on the applications and limitations of the reaction between triorganolead-metal compounds and organic halides.

The cleavage of unsymmetrical organolead compounds by metals was developed as a new and valuable technique for compiling a series of groups which is useful in the prediction of relative reactivities of members of a homologous series.

APPENDIX

A reply from Dr. E. J. Crane to a request for recommendations concerning the nomenclature of certain types of organometallic compounds.

COPY

February 20, 1941

Dr. Ernest Bindschadler,
Iowa State College,
Ames, Iowa.

Dear Dr. Bindschadler:

Dr. Leonard T. Capell of this office and Dr. Austin M. Patterson have been giving some thought to the nomenclature problems discussed by you in your letter of February 1. Doctor Patterson has written with reference to the compounds the following comment:

"I am sorry to have been delayed so long in answering your letter of February 12 about the names of organometallic compounds from Doctor Gilman's laboratory. Several considerations are involved and I wished to avoid too hasty an answer. Even now I do not feel very well prepared to reply, but I realize that Dr. Bindschadler cannot be kept waiting too long. I will accordingly give you my present ideas.

"I see the point in avoiding such names as 'stannide' if possible; it is probably better in such cases to use 'addition' names which are less commital.

"On consideration, I like in most cases the first name for each compound as given in Dr. Bindschadler's list, but I think it might be well to use a hyphen to indicate the closer connection of the organic radicals with one of the metals. At present, then, the names that seem perhaps best to me are:

1.	$(CH_3)_3PbNa$	trimethyllead-sodium
2.	$[(CH_3)_3Pb]_2Ca$	bis(trimethyllead)-calcium
3.	$(C_6H_5)_3PbCaCl$	triphenyllead-calcium monochloride
4.	$(CH_3)_2PbNa_2$	dimethyllead-disodium
5.	$Na(CH_3)_2SnSn(CH_3)_2Na$	tetramethylditin-disodium
6.	$(C_6H_5)_3BNa_2$	triphenylborine-disodium
7.	$(C_2H_5)_3SiNHC_2H_5$	triethyl(ethylamino)silicane (if N-(triethylsilicyl)ethylamine is not acceptable.)

"I have inserted 'mono' in 3 to avoid conveying the impression that it is a compound with $CaCl_2$. Perhaps the

'mono' is not needed. I have substituted 'borine' for 'boron' in 6 and 'silicane' for 'silicon' in 7.

"I would hesitate to coin a whole series of prefixes like calcio-, bario-, etc.; I have never cared specially for sodio- even."

Neither Doctor Capell nor I feel that we can add anything to this discussion.

Sincerely yours,

E. J. Crane
Editor, Chemical Abstracts