CONTRIBUTION FROM THE U. S. ARMY QUARTERMASTER R & E COMMAND, PIONEERING RESEARCH DIVISION, NATICK, MASSACHUSETTS

Synthesis of Organolead Arsonates and Arsinates

BY MALCOLM C. HENRY

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A series of new organolead arsonates, ≡PbOAs(O)O—, and organolead arsinates, ≡PbOAs(O)=, has been prepared. Alternate methods of synthesis are discussed in connection with the relative ease of cleavage of lead–carbon and lead–halogen bonds. The properties of these compounds are discussed.

Organometallic compounds containing M–O–M units (M = metal or metalloid atom) are well known for molecules where M atoms are identical and with M–O–M′ units where M and M′ are dissimilar but of the same group or subgroup in the periodic table. Less well known are compounds containing a group IVA element connected *via* oxygen to a group VA element other than nitrogen, phosphorus, or carbon.

The synthesis of M–O–As type compounds, for example, where M is silicon,[1–3] germanium,[4] or tin[5–7] has been described only recently. The corresponding lead compounds have not been investigated for the case where lead is in its tetravalent state.

Synthesis of Organolead Arsinates.—The metathesis reaction between sodium dimethylarsinate and triphenyllead chloride was successful when effected in refluxing methanol. The same reaction when carried out in benzene resulted in yields of less than 1%, in accordance with the equation

$$(CH_3)_2As(O)ONa + (C_6H_5)_3PbCl \longrightarrow (C_6H_5)_3PbOAs(O)(CH_3)_2 \text{ (I)} + NaCl$$

The monosubstitution product (II) resulting from the reaction of sodium dimethylarsinate with diphenyllead dichloride was insoluble in dimethylformamide.

$$(CH_3)_2As(O)ONa + (C_6H_5)_2PbCl_2 \longrightarrow (C_6H_5)_2(Cl)PbOAs(O)(CH_3)_2 \text{ (II)} + NaCl$$

The insolubility of II in dimethylformamide undoubtedly was reponsible for the fact that longer reaction times in the presence of excess sodium dimethylarsinate failed to produce the disubstituted product.

Ion Cleavage of Tetraphenyllead.—The electronegativity of the group IVA elements is known to vary widely. Relative values for carbon, 2.55; silicon, 1.76; germanium, 1.40; tin, 1.37; and lead, 1.13[8] are related to the observed differences in reactivities of compounds containing group IVA elements bonded directly to carbon. Large differences in reactivity have been noted even between tetraphenyltin and tetraphenyllead and the latter has been reported to be 60 times more sensitive to acid cleavage.[9a,b]

The reaction of tetraphenyllead with HCl is stepwise and can be controlled so as to isolate either the monohalide or the relatively insoluble dihalide.[10] It has not been possible to extend this substitution process to the tri- or tetrahalide. It has been suggested that because of the low dielectric constant of benzene these reactions may take place by a molecular attack of HX on tetraphenyllead.[9a]

Many organolead compounds have been prepared by the reaction of tetrasubstituted lead compounds with mineral or organic acids.[11] The salt-like character of these compounds is suggested by the fact that compounds derived from weak acids generally are more soluble in organic solvents than those formed from strong acids. This is complicated by the case of monosubstituted acid salts of tetraphenyllead because of the sensitivity to cleavage of the second phenyl group by acids to

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(10) H. Gilman and J. D. Robinson, *ibid.*, **51**, 3112 (1929).
(11) R. W. Leeper, L. Summers, and H. Gilman, *Chem. Rev.*, **54**, 101 (1954).

yield the disubstituted acid salts. Triphenyllead chloride, for example, when allowed to react with glacial acetic acid, readily forms diphenylchlorolead acetate. Triphenyllead acetate when allowed to react with dry hydrochloric acid in benzene also forms diphenylchlorolead acetate initially; however, upon further reaction, the acetate ion is displaced to form diphenyllead dichloride, due primarily to the almost complete insolubility of the latter in organic solvents.

Organolead Arsonates.—Two equivalents of benzylarsonic acid when allowed to react with triphenyllead chloride in methanol produced an organolead diarsonate, whereas if propylarsonic acid was used in equivalent molar quantities only the monosubstituted product was obtained, *i.e.*

$$(C_6H_5)_3PbCl + 2C_6H_5CH_2As(O)(OH)_2 \xrightarrow{CH_3OH} (C_6H_5)_2Pb[OAs(O)(OH)CH_2C_6H_5]_2 \text{ (III)} + HCl + C_6H_6$$

or

$$(C_6H_5)_3PbCl + CH_3CH_2CH_2As(O)(OH)_2 \xrightarrow{CH_3OH} (C_6H_5)_2(Cl)PbOAs(O)(OH)CH_2CH_2CH_3 \text{ (IV)} + C_6H_6$$

The use of pyridine as a solvent makes it possible to enhance the reaction by the formation of pyridine hydrochloride. Thus it was possible to synthesize the disubstituted organolead arsonates

$$(C_6H_5)_3PbCl + 2RAs(O)(OH)_2 \xrightarrow{C_5H_5N} (C_6H_5)_2Pb[OAs(O)(OH)R]_2 + C_6H_6 + C_5H_5N\cdot HCl$$

where $R = CH_2{=}CHCH_2$ (V); m-$NO_2C_6H_4^-$ (VI); or $C_6H_5^-$ (VII). A similar reaction starting with tetraphenyllead instead of triphenyllead chloride using *m*-nitrophenylarsonic acid resulted also in the isolation of compound VI

$$(C_6H_5)_4Pb + 2m\text{-}NO_2C_6H_4As(O)(OH)_2 \xrightarrow{C_5H_5N} \text{VI} + 2C_6H_6$$

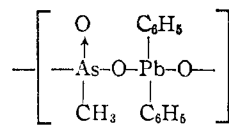
Reaction of triphenyllead chloride and methylarsonic acid in pyridine gave anomalous results. In this case two products, VIII and IX, were isolated, the former containing a ratio of lead to arsenic of 2:1. The second product was apparently the monosubstitution product which upon heating underwent dehydration to form the corresponding anhydride (X). Thus, it is conceivable that the following reaction occurred

$$(C_6H_5)_3PbCl + CH_3As(O)(OH)_2 \longrightarrow [(C_6H_5)_2(Cl)PbO]_2As(O)CH_3 \text{ (VIII)} + (C_6H_5)_2(Cl)PbOAs(O)(OH)CH_3 \text{ (IX)}$$

$$\text{IX} \xrightarrow{-H_2O} [(C_6H_5)_2(Cl)PbOAs(O)(CH_3)]_2O \quad \text{(X)}$$

Reaction between diphenyllead dichloride and disodium methylarsonate in dimethylformamide yields a white powdery material whose analysis indicates a lead–arsenic ratio of 1:1. It was not possible to characterize this compound further, although presumably the initial reaction involves a metathesis to form either a linear chain structure (XI)

$$(C_6H_5)_2PbCl_2 + CH_3As(O)(ONa)_2 \longrightarrow$$



—(XI) + NaCl

or a cyclic dimer (XII)

$$(C_6H_5)_2Pb{<}(O\text{–}As(O)(CH_3)\text{–}O)_2{>}Pb(C_6H_5)_2 \text{ (XII)}$$

Reaction of Organolead Arsonates with Glacial Acetic Acid.—The reaction of organolead arsonates with glacial acetic acid makes it possible to replace the arsonate groups by acetate, yielding in these cases either diphenyllead diacetate or diphenylchlorolead acetate. This reaction quickly determines whether a mono- or disubstitution has taken place since diphenyllead diacetate crystallizes from glacial acetic acid upon standing and can be easily identified, whereas diphenylchlorolead acetate decomposes before melting and is insoluble in glacial acetic acid.

Since a minimum of two phenyl groups are assumed to be attached to the lead atom and since elemental analyses determine the lead-to-arsenic ratio, it is possible to identify all four groupings attached to the central lead atom. In the absence of this reaction, it is possible to have a Pb:As ratio of 1:1 and three possible configurations, either the monosubstituted $(C_6H_5)_2ClPbOAs(O){=}$, the disubstituted cyclic product $(C_6H_5)_2Pb{<}[OAs(O)(R)O]_2{>}Pb(C_6H_5)_2$, or a polymer. In its simplest sense this reaction with glacial acetic acid may be considered as a qualitative test for the presence of chloride.

These compounds, having no melting points up to 260°, all are insoluble in the common organic solvents, thus making purification difficult. As a result the elemental analyses are, more often than not, unacceptable by normal standards. It is felt, however, that they are sufficiently definitive to establish the identity of the compounds described. It was not possible to ascertain whether inter- or intramolecular dehydration was responsible for the deviations noted. The infrared spectra of these compounds indicate that in certain cases this may be the case. Investigations currently are being carried out to clarify this point.

Infrared Studies.—Our studies have shown that the infrared spectra of organoarsonic acids have some useful absorptions which are pertinent to this investigation. Methyl-, phenyl-, benzyl-, β-chlorovinyl-, allyl-, propyl-, *m*-nitrophenyl-, *p*-hydroxyphenyl-, and butylarsonic acids all show intense broad absorptions at *ca.* 2702 and 2381–2272 cm.$^{-1}$ using potassium bromide pelleting techniques. It is assumed these absorptions are associated with the OH stretching vibrations, since these absorption bands are absent in the cases of triphenylarsine, arsenic trioxide, and methylarsine oxide.

Infrared absorption characteristic for aromatic compounds of lead appears as an intense narrow band at 1058 cm.$^{-1}$.[12] We have noted this band to be invariant for a large number of organolead compounds containing two to four phenyl groups. Other atoms attached to lead such as halogens or sulfur do not change the intensity of the absorption. During the course of this investigation, however, it was noted that with aryllead acetates and aryllead arsonates, that is, where there exists a Pb–O bond, the intensity of the 1058 cm.$^{-1}$ absorption decreases markedly and in some cases almost disappears. Aryltin compounds have an analogous absorption at 1070 cm.$^{-1}$ and it has been noted that in the case of aryltin arsonates this absorption also decreases and almost disappears.[3]

In general, the organolead arsonates show absorption bands in the 750–950 cm.$^{-1}$ region which are absent in the starting materials. These bands presumably are associated with the Pb–O–As bonds. These bands are intense, sometimes multiple in nature, and broad. In the case of the organotin arsonates, new, intense, broad bands in the same general area of the spectrum are characteristic.[3]

The triphenyllead derivative of dimethylarsinic acid (compound I) shows two intense bands at 875 and 834 cm.$^{-1}$, whereas the diphenylchlorolead derivative, compound II, shows an intense band at 790 cm.$^{-1}$ that predominates the spectrum. Both compounds show the expected methyl and phenyl vibrations plus a weak phenyl–Pb absorption at 1058 cm.$^{-1}$.

(12) J. G. Noltes, M. C. Henry, and M. J. Janssen, *Chem. Ind.* (London), 298 (1959).

Table I summarizes the infrared spectra of the organolead arsonates (cm.$^{-1}$). Column A lists the absorption bands formed which are present in the product but not in the reactants. Column B lists absorptions that have disappeared, but which were present in the parent arsonic acid.

TABLE I

Compound	Organolead arsonate (formed), cm.$^{-1}$	Parent arsonic acid (disappeared), cm.$^{-1}$
III	875, 855, 1015	865, 2702, 2280
VII	853	880, 778
IV	870, 800	770, 915, 1220, 2702, 2280
VI	833, 750	768
V	890	775, 1220
VIII	768, 840, 870, 880	{780, 940, 1215, 2702, 2280
IX	815, 842, 870, 883	
X		
XI	770, 790	733, 820, 3350

The formation of intense bands between 770 and 870 cm.$^{-1}$ appears to be characteristic of Pb–O–As type compounds. Comparison with Sn–O–As spectra seems to indicate this latter structure absorbs between 800 and 900 cm.$^{-1}$. It should be realized that until more data are available these absorptions should not be interpreted as other than empirical characteristics of the products.

Experimental

Melting points were taken with a Kofler hot stage. Organolead starting materials and reference materials tetraphenyllead,[13] triphenyllead chloride and diphenyllead dichloride,[10] triphenyllead iodide, triphenyllead acetate,[14] and diphenyllead diacetate[15] were prepared by published methods. The organosubstituted arsonic acids were generously supplied by American Smelting & Refining Co., Rahway, N. J., through the late R. Kary. Infrared spectra were obtained using a Perkin-Elmer Infracord spectrophotometer.

Triphenyllead Dimethylarsinate (I).—Sodium cacodylate trihydrate (Mallinckrodt) (10 mmoles) and triphenyllead iodide (10 mmoles) dissolved in 200 ml. of methanol were refluxed for 8 hr. The methanol was evaporated, the residue washed with water several times, and finally recrystallized twice from methanol; yield, pure triphenyllead dimethylarsinate, 4.2 g. (73%).

Anal. Calcd. for $C_{20}H_{21}AsPbO_2$: C, 41.74; H, 3.65; Pb, 36.05; As, 13.04. Found: C, 41.58; H, 3.71; Pb, 35.20; As, 13.02.

The same reaction was carried out, as described above, in benzene; after 50 hr. reflux only 0.3 g. of triphenyllead dimethylarsinate was produced.

Triphenyllead dimethylarsinate refluxed together with excess glacial acetic acid produced diphenyllead diacetate

(13) H. Gilman and J. Robinson, *J. Am. Chem. Soc.*, **49**, 2315 (1927).

(14) R. Heap and B. C. Saunders, *J. Chem. Soc.*, 658 (1951).

(15) A. Polis, *Ber.*, **20**, 3331 (1887).

quantitatively. The product was identified by mixed melting point with an authentic sample and comparison of infrared spectra of an authentic sample.

Diphenylchlorolead Dimethylarsinate (II).—Diphenyllead dichloride (10 mmoles), together with sodium cacodylate trihydrate (20 mmoles), was dissolved in 300 ml. of dimethylformamide and refluxed for 8 hr. A white insoluble precipitate formed on the sides of the flask during the reaction period. The precipitate was filtered, washed with several aliquots of water, and dried; yield, 4.1 g. (76.9%) of diphenylchlorolead dimethylarsinate.

Anal. Calcd. for $C_{14}H_{16}O_2AsClPb$: C, 31.50; H, 3.00; Pb, 38.90; As, 14.03. Found: C, 30.83; H, 3.15; Pb, 39.00; As, 13.06.

An aliquot of diphenylchlorolead dimethylarsinate refluxed for several minutes with excess glacial acetic acid produced diphenylchlorolead acetate quantitatively.

Diphenyllead Bis-(benzylarsonate) (III).—Triphenyllead chloride (5 mmoles), together with benzylarsonic acid (10 mmoles), was dissolved in 400 ml. of methanol and refluxed for 16 hr. A white insoluble precipitate was produced. Filtration and washing with fresh solvent yielded 2.6 g. (35%) of diphenyllead bis-(benzylarsonate).

Anal. Calcd. for $C_{26}H_{26}O_6As_2Pb$: C, 39.50; H, 3.30; As, 18.90; Pb, 26.19. Found: C, 40.13; H, 3.81; As, 18.39; Pb, 25.9.

Reaction with glacial acetic acid produced diphenyllead diacetate.

Diphenylchlorolead Propylarsonate (IV).—Triphenyllead chloride (5 mmoles), together with propylarsonic acid (5 mmoles), dissolved in 300 ml. of methanol and refluxed 12 hr. produced a white insoluble precipitate. Filtration and washing with successive portions of methanol and water yielded diphenylchlorolead propylarsonate, 2.5 g. (89% yield).

Anal. Calcd. for $C_{16}H_{18}O_3AsClPb$: C, 31.90; H, 3.20; As, 13.30; Pb, 36.80. Found: C, 31.40; H, 3.64; As, 13.37; Pb, 38.7.

Reaction with glacial acetic acid produced diphenylchlorolead acetate.

Diphenyllead Bis-(allylarsonate) (V).—Allylarsonic acid (10 mmoles), together with triphenyllead chloride (5 mmoles), was dissolved in 250 ml. of pyridine and heated at 70° for 24 hr. Cooling produced 2 g. of colorless crystals. Filtration and washing of the residue left 2.0 g. of diphenyllead bis-(allylarsonate), 35.4% yield.

Anal. Calcd. for $C_{18}H_{22}O_6As_2Pb$: C, 31.26; H, 3.19; As, 21.68; Pb, 30.00. Found: C, 30.91; H, 3.32; As, 21.72; Pb, 30.00.

Reaction with glacial acetic acid produced diphenyllead diacetate.

Diphenyllead Bis-(*m*-nitrophenylarsonate) (VI): *m*-Nitrophenylarsonic acid (10 mmoles), together with triphenyllead chloride (5 mmoles) in 300 ml. of pyridine, was heated at 70° for 24 hr. The pale yellow crystals that gradually formed during the reaction were filtered, washed with pyridine and methanol, and dried under vacuum; yield, 2.3 g. (53.8%) diphenyllead bis-(*m*-nitrophenyl arsonate).

Anal. Calcd. for $C_{24}H_{20}O_{10}As_2N_2Pb$: C, 33.76; H, 2.64; As, 17.54; Pb, 24.29. Found: C, 33.30; H, 2.65; As, 17.40; Pb, 23.85.

Reaction with glacial acetic acid produced diphenyllead diacetate. (An alternate synthesis of VI was carried out using tetraphenyllead and *m*-nitrophenylarsonic acid with a similar stoichiometry of 1:2. The reaction was carried out in pyridine at 70° for 6 hr. and the product (VI) isolated as described above.)

Diphenyllead Bis-(phenylarsonate) (VII).—Phenylarsonic acid (10 mmoles), together with triphenyllead iodide (5 mmoles), dissolved in pyridine was heated 18 hr. at 80°. Upon standing overnight white crystals separated out of solution. Filtration and air drying yielded 1.5 g. (32.6%) of the dipyridine complex of diphenyllead bis-(phenylarsonate).

Anal. Calcd. for $C_{34}H_{32}O_6As_2N_2Pb$: C, 44.29; H, 3.58; As, 16.26; N, 3.03; Pb, 22.49. Found: C, 43.71; H, 3.49; As, 16.55; N, 2.91; Pb, 22.29.

An aliquot of the dipyridine complex boiled for 1 hr. with anhydrous methanol destroyed the complex to yield diphenyllead bis-(phenylarsonate).

Anal. Calcd. for $C_{24}H_{22}O_6As_2Pb$: C, 37.74; H, 2.89; As, 19.63; Pb, 27.10. Found: C, 38.84; H, 3.38; As, 19.61; Pb, 26.1.

A second aliquot of the pyridine complex boiled for several minutes with glacial acetic acid yielded diphenyllead diacetate.

Anal. Calcd. for $C_{16}H_{16}PbO_4$: C, 40.08; H, 3.34; Pb, 43.25. Found: C, 40.08; H, 3.36; Pb, 43.20.

Reaction of Triphenyllead Chloride and Methylarsonic Acid.—Methylarsonic acid (0.02 mole) and triphenyllead chloride (0.02 mole) were dissolved in 200 ml. of pyridine and stirred for 12 hr. in an oil bath maintained at a temperature of 80–90°. The white crystalline plates that formed during the reaction were filtered and washed with chloroform; yield, 9.5 g. (88.7%) of diphenylchlorolead monobasic ester of methylarsonic acid (IX).

Anal. Calcd. for $C_{13}H_{14}O_3AsClPb$: C, 29.05; H, 2.61; As, 13.95; Pb, 38.6. Found: C, 28.74; H, 2.86; As, 13.62; Pb, 38.4.

Reaction with glacial acetic acid produced diphenylchloroacetate. Compound IX boiled in methanol for 30 min. slowly produced a precipitate no longer soluble in the solvent. This appears to be the corresponding anhydride compound X.

Anal. Calcd. for $C_{26}H_{26}O_5As_2Cl_2Pb_2$: C, 29.60; H, 2.47; As, 14.3; Pb, 39.3. Found: C, 29.59; H, 2.81; As, 14.05; Pb, 39.7.

Reaction with glacial acetic acid produced diphenylchlorolead acetate.

Evaporation of the original pyridine solution yielded a white powder which after washing with chloroform yielded 1.49 g. of a product which contains lead and arsenic in the ratio of 2:1. A compound such as compound VIII seems probable.

Anal. Calcd. for compound VIII ($C_{25}H_{23}O_3AsCl_2Pb_2$): C, 32.20; H, 2.47; As, 7.95; Pb, 44.5. Found: C, 30.32; H, 2.90; As, 7.88; Pb, 41.2.

Reaction with glacial acetic acid produced diphenylchlorolead acetate.

Reaction of Diphenyllead Dichloride and Disodium Methylarsonate.—Diphenyllead dichloride (0.01 mole) and disodium methylarsonate (0.01 mole) were dissolved in dimethylformamide and refluxed for 8 hr. During the reaction a white powdery precipitate gradually formed. The precipitate, filtered and washed with fresh solvent several times, yielded 6.0 g. of product insoluble in common organic solvents.

Anal. Calcd. for $(C_{13}H_{13}O_3AsPb)_x$ (XI or XII): C, 31.3; H, 2.61; As, 15.0; Pb, 41.5. Found: C, 28.48; H, 2.72; As, 13.87; Pb 41.8.

This product boiled together with glacial acetic acid yielded diphenyllead diacetate.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA

The Determination of Complex Formation in Mixed Solvents by Gas Chromatography. The Tetrahydrofuran Complexes of Lithium Aluminum Hydride, Magnesium Bromide, and Several Grignard Reagents[1]

BY LLOYD V. GUILD, C. A. HOLLINGSWORTH, DARL H. McDANIEL,[2] AND SUNIL KUMAR PODDER

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A gas chromatographic method has been used to obtain relative partial pressures of solutions containing mixed volatile solvents. The data, analyzed by a method previously used by McCauley, *et al.*, yield the stoichiometry of complexes formed by tetrahydrofuran with ethyl ether solutions of lithium aluminum hydride, magnesium bromide, and several Grignard reagents. The complexes indicated are $LiAlH_4 \cdot 2THF$, $R_2Mg \cdot MgBr_2 \cdot 2THF$, and $MgBr_2 \cdot 3/2THF$. A dioxane complex $R_2Mg \cdot MgBr_2 \cdot 2C_4H_8O_2$ also is indicated. The latter two are apparent complexes existing in heterogeneous mixtures of liquid and solid.

The partial pressures exerted by volatile components in a multicomponent system provide a direct measure of the activity of the volatile components. Conclusions regarding complexing between a given volatile component and other components of the system may be made by analysis of the appropriate partial pressure–composition isotherms. One of the most direct methods of analysis of such data is the determination of the displacement of the partial pressure–composition isotherm in the presence, and in the absence, of a solute.[3] The previous studies were carried out using vacuum line systems and involved direct manometric measurements. Since only the total pressure was measured, application has been limited to those systems in which the complexing agent is the only appreciably volatile component in the system. The use of gas chromatography for the determination of relative partial pressures removes the restriction that only the complexing agent be appreciably volatile.

A constant volume, constant temperature, sample of a vapor in equilibrium with a solution contains an amount of each component of the solution which is proportional to the partial pressure of each component. The gas chromatogram of the sample will have a peak area for a given component (or for symmetrical peaks, a peak height) which will be proportional to the amount of that component. Thus the chromatogram for a constant volume, constant temperature, sample will have an area (or peak height) which will be directly proportional to the partial pressure of the component giving the peak.

Experimental

Apparatus.—A diagram of the apparatus used is shown in Fig. 1. It consisted of a manostated reflux vessel, gas sampling valve, and a gas chromatograph.

A prototype of the Burrell Model K-5 gas chromatograph was used. Polypropylene glycol, supported on diatomaceous earth, was used as a column packing; the col-

(1) Based in part on a thesis submitted by L. V. Guild in June, 1960, in partial fulfillment of the requirements for the degree of Master of Science.

(2) Chemistry Department, University of Cincinnati, Cincinnati, Ohio.

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