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Part IX.^{1,2} The Preparation and Reactions of **Organometallic Reactions.** Trialkyl-lead Alkoxides

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A number of trialkyl-lead alkoxides have been prepared by treating the corresponding lead halide with a sodium alkoxide, or lead hydroxide (or methoxide) with an alcohol.

These alkoxides undergo substitution reactions with phthalic anhydride giving alkyl trialkyl-lead phthalates, and with chloroform, bromoform, and cyclopentadiene to yield trihalogenomethyl- and cyclopentadienyl-lead compounds.

The alkoxides add to multiply-bonded reagents such as isocyanates, carbodi-imides, isothiocyanates, carbon disulphide, carbon dioxide, trichloroacetonitrile, acrylonitrile, and chloral, to give 1:1-adducts. The adducts with hexachloroacetone and bromal decompose at room temperature, providing an alternative route to the trihalogenomethyl-lead compounds.

MANY studies have been reported recently of the preparation, physical properties, and chemical reactions of trialkyltin alkoxides. The principal routes by which these compounds can be prepared are illustrated in equations (1),³ (2),⁴ (3),⁵ and (4) ⁵ (M = Sn, X = halide). The Sn-O bond in the product very readily takes part in substitution and addition reactions, providing a basis for some useful synthetic and catalytic procedures.⁶

$$R^{1}_{3}MX + NaOR^{2} \longrightarrow R^{1}_{3}M OR^{2} + NaX \qquad (1)$$

$$R^{1}_{3}M \cdot OR^{3} + HOR^{2} \longrightarrow R^{1}_{3}M \cdot OR^{2} + HOR^{3}$$
(2)

$$(R_{3}^{1}M)_{2}O + HOR^{2} \longrightarrow R_{3}^{1}M OR^{2} + H_{2}O$$
(3)

$$(R_{3}^{1}M)_{2}O + OC(OR^{2})_{2} \longrightarrow R_{3}^{1}M \cdot OR^{2} + CO_{2}$$
(4)

In contrast, very little is known of the trialkyl-lead alkoxides.⁷ Triethyl-lead methoxide,⁸ ethoxide,^{8,9} and dimethylphenylmethoxide ⁸ were reported to be unstable, and to decompose in sealed ampoules at room temperature. The only systematic study appears to be that by Amberger and Hönigschmid-Grossich,¹⁰ who prepared the methoxides R_3Pb ·OMe (R = Me, Et, Pr, and Bu) by treating the appropriate trialkyl-lead chloride with sodium methoxide in ether or tetrahydrofuran. The products were solids that could be purified by sublimation under reduced pressure, but which decomposed fairly rapidly on storage. No reactions of the alkoxides have been described.*

This Paper describes an investigation of the relative merits of reactions (1)—(4) (M = Pb) for preparing organolead alkoxides. Some simple substitution and addition reactions of the alkoxides are also reported.

The Preparation of Trialkyl-lead Alkoxides.—The

* It is surprising that as much is known about the trialkyllead alkyl peroxides (R13Pb.O.OR2) as about the alkoxides. Some eight of these peroxides have been prepared by reactions analogous to those of equations (1)—(3).¹¹

¹ Part VIII, A. G. Davies and P. G. Harrison, J. Chem. Soc. (C), 1967, 1313. ² A preliminary Note on the present work has appeared:

. G. Davies and R. J. Puddephatt, J. Organometallic Chem., 1966, **5**, 590.

³ D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, **1962**, **2050**. ⁴ G. P. Mack and E. Parker, U.S.P., **2727917** (*Chem. Abs.*, 1956, 50, 10,761).

A. G. Davies, P. R. Palan, and S. C. Vasishtha, Chem. and

⁶ A. G. Davies, 1. 14. 1 and 1.
⁷ Ind., 1967, 229.
⁶ Part VII, A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, J. Chem. Soc. (C), 1967, 1309.

alkoxides which were prepared are shown in the Table, where the preparative method is numbered to correspond with the appropriate equation.

The methoxides were best obtained by treating the organo-lead chloride or bromide in ether or tetrahydrofuran with sodium methoxide in methanol (equation 1, M = Pb). The sodium halide was precipitated immediately; after 30 min. it was centrifuged off, and the lead methoxide was purified by sublimation. This is essentially the same procedure as that followed by Amberger and Hönigschmid-Grossich,¹⁰ except that these authors apparently used sodium methoxide which was free from methanol, and stirred the reaction mixture for 10-24 hr.

Higher alkoxides can be prepared by the same method, but we found it more convenient to carry out the alcoholysis of the methoxide (equation 2; M = Pb, $R^3 = Me$), usually with an excess of the appropriate alcohol. Alternatively, these alkoxides can be prepared by azeotropic dehydration of a mixture of the trialkyllead hydroxides and alcohol in benzene or toluene (equation 3; M = Pb), but the hydroxides are normally prepared from the halides, and indeed the pure hydroxides are probably best obtained by hydrolysis of the methoxides.

The reaction between the trialkylmetal oxide or hydroxide, and a dialkyl carbonate (equation 4), which provides the best route to the trialkyltin derivatives of the lower alcohols,⁵ is not convenient for the preparation of trialkyl-lead alkoxides. When triethyl- or triphenyl-lead hydroxide and dimethyl carbonate were heated together, only bistrialkyl-lead carbonate was isolated. Bistriphenyl-lead oxide appeared to react with dimethyl

7 Organolead chemistry has been reviewed by R. W. Leeper, L. Summers, and H. Gilman, Chem. Rev., 1954, 54, 101, and L. C. Willemsens 'Organolead Chemistry,' International Lead Zinc Research Organisation, New York, 1964. ⁸ Yu. A. Aleksandrov, T. G. Brilkina, and V. A. Shushunov,

Doklady Akad. Nauk, 1961, 139, 89. 9 H. Gilman, S. M. Spatz, and M. J. Kolbezen, J. Org. Chem.,

1953, 18, 1341.

¹⁰ E. Amberger and R. Hönigschmidt-Grossich, Chem. Ber., 1965, 98, 3795.

 ¹¹ (a) Yu. A. Aleksandrov, T. G. Brilkina, and V. A. Shushunov, Trudy po Khim. i Khim. Tekhnol., 1960, 3, 381 (Chem. Abs., 1961, 55, 27,023); (b) A. Rieche and J. Dahlmann, Monatsber. Deut. Akad. Wiss., Berlin, 1959, 1, 491; Annalen, 1964, 675, 19;
 (c) revised by: C. Secretardy and L. H. Brunn, Chem. Part 1966. (c) reviewed by G. Sosnovsky and J. H. Brown, Chem. Rev., 1966, **66**, 529.

carbonate in boiling toluene to give a mixture of triphenyl-lead methoxide and bistriphenyl-lead carbonate. As the lead hydroxides or oxides are not readily available as starting materials, these reactions were not investigated further.

The trialkyl-lead alkoxides are liquids or solids that can usually be purified by distillation or sublimation; trimethyl-lead 2,2-dimethylpropoxide, isopropoxide, and t-butoxide, and triethyl-lead benzyl oxide, however, could not be volatilised below their decomposition temperatures. The lead alkoxides are much less stable than the corresponding organotin compounds; melting is often accompanied by decomposition and blackening, and they develop a black colour after a few days even in a sealed tube at room temperature. The proton magnetic resonance spectrum showed that the major product when triethyl-lead methoxide decomposed in carbon tetrachloride, was tetraethyl-lead. The only common organotin alkoxide which decomposes similarly is trimethyltin methoxide which, on heating, gives tetramethyltin and dimethyltin dimethoxide. Triphenyllead methoxide, in contrast, could not be sublimed, and did not decompose at room temperature.

The trialkyl-lead alkoxides are soluble in common organic solvents. They are all hydrolysed very rapidly in the air, yielding the trialkyl-lead hydroxides: these are more basic than the bistrialkyltin oxides, and the organolead alkoxides can be estimated by titration with standard acid (see the Table).

In the infrared spectra, the lead alkoxides showed a strong C-O stretching vibration (see the Table). In the methoxides, this was at 1035-1042 cm.⁻¹ (cf. ref. 10), but shifted to higher frequency (1042-1080 cm.⁻¹) in the alkoxides derived from the higher alcohols; exceptionally, the C-O vibration in triethyl-lead isopropoxide, 1-phenylethoxide, and t-butoxide, was at 1121, 1153, and 1191 cm.⁻¹, respectively. The trialkyltin alkoxides usually show a C-O stretching vibration in the range 1050-1080 cm.⁻¹.

The τ values for the O-CH_n group in the n.m.r. spectra are also recorded in the Table In no case was coupling apparent between ²⁰⁷Pb and O-CH_n at 33° . This contrasts with the coupling which can often be observed between 117/119Sn and O-CH_n in the corresponding tin alkoxides under the same conditions, and probably indicates that intermolecular exchange of alkoxy-groups occurs relatively rapidly in the organolead compounds.

Reactions of the Type $R^{1}_{3}Pb \cdot OR^{2} + A - B \longrightarrow$ $R_{3}^{1}PbA + BOR^{2}$.—The metal-oxygen bond of metal alkoxides, hydroxides, and oxides, reacts metathetically with reagents $A^{\delta}-B^{\delta+}$ by nucleophilic attack of oxygen upon B, and of A upon the metal. Examples of such processes have already been given in the previous section in the reaction of organolead hydroxides with alcohols

13 A. G. Davies and T. N. Mitchell, J. Organometallic Chem., 1966, **6**, 568.

and with dimethyl carbonate, and of alkoxides with alcohols and with water, and in the postulated exchange of alkoxy-groups between different lead sites. This section describes some further reactions of the Pb-O bond which are useful preparatively.

Triethyl-lead methoxide reacts exothermically with phthalic anhydride in benzene to give crystalline methyl triethyl-lead phthalate (equation 5). Similar reactions have been established previously for the trialkyltin alkoxides,¹² and provide derivatives which are useful for characterising the metal alkoxides.

Trialkyltin dialkylamides have been shown to react rapidly with haloforms at room temperature to give the corresponding trialkyltrihalogenomethyltins,13 but the trialkyltin alkoxides are inert under the same conditions. The lead-oxygen bond, however, is more reactive in acidolysis than the tin-oxygen bond, and triphenyl-lead methoxide reacts with chloroform and with bromoform at room temperature to give the corresponding trihalogenomethyltriphenyl-lead (equation 6, X = Cl or Br).

$$Ph_{3}Pb OMe + X_{3}CH \longrightarrow Ph_{3}Pb CX_{3} + HOMe$$
 (6)

A similar reaction, which is now very exothermic, occurs between triethyl-lead methoxide and the same two haloforms, but the products are oils which are too unstable to be purified.

The only other metal alkoxides that are known to give isolable trihalogenomethyl compounds with haloforms are the mercuric alkoxides; ¹⁴ the alkoxides of Group I metals, for example potassium t-butoxide, react with haloforms, but the trihalogenomethylmetallic compounds are then only transient intermediates which decompose into metal halide and dihalogenocarbene.

Trichloromethyltriphenyl-lead (m. p. 171-171.5°) and tribromomethyltriphenyl-lead (m. p. 135-140°) have also been obtained from the reaction of triphenyllead methoxide with hexachloroacetone and with tribromoacetaldehyde, respectively (see below),² and Willemsens and van der Kerk prepared trichloromethyltriphenyl-lead (m. p. 169-170°) by treating triphenylplumbyl-lithium with carbon tetrachloride.¹⁵

Trialkyltin dialkylamides similarly react with cyclopentadiene to give the corresponding cyclopentadienyltin compounds.¹⁶ The parallel between the reactivity of the Sn-N and the Pb-O bonds again holds, and triethyllead methoxide and cyclopentadiene react rapidly forming cyclopentadienyltriethyl-lead.

Reactions of the Type $R^1_3Pb \cdot OR^2 + A = B \longrightarrow$ R¹₃Pb·A·B·OR².---Metallic derivatives M-X which react

¹² A. J. Bloodworth, unpublished work.

¹⁴ G. Holan, Tetrahedron Letters, 1966, 1985.

¹⁵ L. C. Willemsens and G. J. M. van der Kerk, 'Investigations in the Field of Organolead Chemistry,' International Lead Zinc Research Organisation, New York, 1965, pp. 42, 98. ¹⁶ K. Jones and M. F. Lappert, *J. Organometallic Chem.*, 1965, 2005.

^{3, 295.}

metathetically with singly bonded reagents A-B, will also react additively with appropriate multiply-bonded compounds A=B.¹⁷ At the time when the present work was started, the Sn-O bond of organotin oxides and alkoxides,¹⁸ and the Sn-N bond of organotin amides ¹⁹ had been shown to add to reagents such as isocyanates, isothiocyanates, aldehydes, carbodi-imides, and ketens,

The trialkyl-lead alkoxides gave adducts which were usually oils and which decomposed with blackening during a few days at room temperature; the compounds could not be purified by distillation. These adducts were usually characterised through their infrared and n.m.r. spectra by comparison with the corresponding analytically pure organotin compounds; frequently, the products

Trialkyl-lead alkoxides

					A COULT / LOUGE COUL	01110-00							
					-			Found			Required		
		Prep.	Yield			τ	$\nu_{\rm max.}$ (cm, -1)			Equiv.			Equiv.
	R ¹ ₃ Pb•OR ²	method	(%)	M. p.ª	B. p. ^d (mm.)	(OCH_n)	(C-O)	С	\mathbf{H}	wt.	С	н	wt.
1	Me ₃ Pb·OMe	1	67	ca. 250° (d) e	$70-100^{\circ}(s)$ (0.05)	6.44	1042	16.3	$3 \cdot 9$	289	17.0	$4 \cdot 3$	283
2	Me ₃ Pb•OEt	2	38	$113 - 115^{\prime}$	60	$6.20(4)^{k}$	1044	14.1	$3 \cdot 6$	297	20.2	4.7	297
3	Me ₃ Pb•OPr	2	74	128 - 131	70-100(s)(0.3)	6·30 (3) *	1054	$22 \cdot 2$	4 ·8	306	23.0	$5 \cdot 1$	311
4	Me ₃ Pb·OPe •	3		Liquid	(d)	6-46 ^k							
5	Me ₃ Pb•OPr ⁱ	3		Solid	(d)	$5.93(7)^{k}$				293			311
6	Me ₃ Pb·OBu ^t	3		Solid	(d)	k				276			325
7	Et ₃ Pb•OMe	1	71	81 - 83 f	50 - 80(s) (0.05)	6.29	1042	25.6	5.9	334	$25 \cdot 8$	$5 \cdot 5$	325
8	Et ₃ Pb·OEt	2	86	37 - 39 g	51 - 53 (0.04)	6·41 (4)	1050	28.0	5.7	346	28.3	$5 \cdot 9$	339
9	Et ₃ Pb•OPr	2	57		74-76 (0.2)	6.25(3)	1064	31.8	6.7	360	30.5	$6 \cdot 2$	353
10	Et ₃ Pb•OBu	2	80		78-79 (0.05)	6.21(3)	1072	$33 \cdot 1$	$6 \cdot 9$	371	32.7	$6 \cdot 5$	367
11	Et ₃ Pb·OBu ⁱ	2	85		5658 (0·1)	6.43(2)	1062	32.5	6.7	383	32.7	6.5	367
12	Et _a Pb•OPe ^a	2	59		107 - 110(0.1)	6.57	1071	34.0	6.7	398	34.5	6.8	381
13	Et ₃ Pb·OPr ⁱ	2	73		48-50 (0.05)	5.88 (7)	1121	30.6	$6 \cdot 3$	369	30.5	6.2	353
14	Et ₃ Pb·OC ₆ H ₁₁ ^b	3	82		<110(0.1)	6·42 ^j		38.8	$7 \cdot 1$	436	36.6	6.6	393
15	Et ₃ Pb·OCH(Me)Ph	3	62		<110 (0.05)	5.01	1153			550			415
16	Et ₃ Pb·OBu ^t	2	84		58-60 (0.2)		1191	$32 \cdot 3$	6.7	375	32.7	6.5	367
17	Bu ₃ Pb•OMe	1	79	46-48 h	. ,	6.45	1040	47.0	$3 \cdot 7$		48.5	$3 \cdot 8$	
18	Ph ₃ Pb•OMe	1	95	9091		6.56	1035	36.5	$7 \cdot 0$	494	38.1	$7 \cdot 3$	469
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^a Pe = 2,2-Dimethylpropyl. ^b C₆H₁₁ = Cyclohexyl. ^c d = Decomposition. ^d s = Sublimation. ^e M.p. 250–260° (d)¹⁰. ^f M. p. 60–70°,⁸ 81–83°; ¹⁰ b. p. 50–70°(s)/0.02 mm.¹⁰ ^g M. p. 20°.⁸ ^h M. p. 55–56°; b. p. 70–100°(s)/0.02 mm.¹⁰ ⁱ When H_a-H_β coupling occurs in OR, the centre of the H_a multiplet is quoted, with the number of component peaks in parentheses. In every case, J_{Ha} -H_β = 6.0–7.5 c./sec. ^j Broad. ^k Compound, τ (CH₃Pb), $J_{\text{Pb-CH}_3}$ (c./sec.): (1) 8.82, 75.6; (2) 8.72, 72.6; (3) 8.84, 68·4; (4) 8·68, 70·8; (5) 8·77, 69·6; (6) 8·80, 68·4.

but no additions involving the Pb-O or Pb-N bonds had been demonstrated.

Recently, however, Willemsens and van der Kerk²⁰ have established the oxyplumbylation of keten in the reactions shown in equations (7) and (8).

$$\begin{array}{l} Ph_{3}Pb \cdot OAc + CH_{2}=C=O + EtOH \longrightarrow Ph_{3}Pb \cdot CH_{2} \cdot CO_{2}Et \quad (7) \\ 2Ph_{3}Pb \cdot OH + 4CH_{2}=C=O \longrightarrow (Ph_{3}Pb \cdot CH_{2} \cdot CO)_{2} + \\ & (CH_{3} \cdot CO)_{2}O \quad (8) \end{array}$$

Neumann and Kühlein have reported the reaction of tributyl-lead diethylamide with a number of acceptor molecules.²¹ Isocyanates and benzonitrile gave 1:1adducts, and could be converted into the cyclic trimers. Allyl isothiocyanate, dicyclohexylcarbodi-imide, and some aldehydes underwent simple 1,2-addition, and phenyl isocyanide and benzylidene malononitrile reacted by 1,1- and 1,4-addition, respectively. These authors have also reported the (1,2-)addition of tributyl-lead hydride to acrylonitrile, methyl acrylate, styrene, phenyl isocyanate, and phenylacetylene.²²

We have investigated the reaction of the lead alkoxides with the same acceptor molecules that were used for the trialkyltin alkoxides. The reactivity generally followed the same sequence in addition and in substitution, *i.e.*, $\mathrm{R}^{1}_{3}\mathrm{Pb}\text{\cdot}\mathrm{OR}^{2}\sim\mathrm{R}^{1}_{3}\mathrm{Sn}\text{\cdot}\mathrm{NR}^{2}_{2}>\mathrm{Ar}_{3}\mathrm{Pb}\text{\cdot}\mathrm{OR}^{2}>\mathrm{R}^{1}_{3}\mathrm{Sn}\text{\cdot}\mathrm{OR}^{2}.$

17 M. F. Lappert and B. Prokai, Adv. Organometallic Chem., 1967, 5, 225.

 A. G. Davies, Trans. N.Y. Acad. Sci., 1964, 26, 923.
 T. A. George, K. Jones, and M. F. Lappert, J. Chem. Soc., 1965, 2157.

of hydrolysis were isolated. The adducts formed by triphenyl-lead methoxide, on the other hand, were thermally stable solids which were less readily hydrolysed, and frequently could be purified by recrystallisation.

1-Naphthyl isocyanate reacted rapidly and exothermically with triphenyl-lead methoxide and tributyl-lead methoxide giving the corresponding plumbylcarbamates which could readily be hydrolysed to methyl N-1naphthylcarbamate (equation 9). Triethyl-lead 1phenylethoxide, which could not be purified by distillation, was treated with phenyl isocyanate, and characterised as 1-phenethyl N-phenylcarbamate.

$$R_{3}Pb \cdot OMe + 1 \cdot C_{10}H_{7}NCO \longrightarrow R_{3}Pb \cdot N(1 \cdot C_{10}H_{7})CO \cdot OMe \xrightarrow{H_{2}O} 1 \cdot C_{10}H_{7}NH \cdot CO \cdot OMe \quad (9)$$

Both the tributyl- and triphenyl-plumbylcarbamates were approximately monomolecular in dilute solution in benzene. The tributylplumbyl compound was the less hydrolytically and thermally stable, and a sample in a sealed tube turned brown after a few days. Both gave a band in the infrared spectrum (Nujol mull) at 1640 cm.⁻¹, whereas the corresponding trialkylstannylcarbamates usually give a doublet in the region 1635-1690 cm.⁻¹

²⁰ L. C. Willemsens and G. J. M. van der Kerk, J. Organometallic Chem., 1965, 4, 241.

²¹ W. P. Neumann and K. Kühlein, Tetrahedron Letters, 1966, 3423.

²² W. P. Neumann and K. Kühlein, Angew. Chem. Internat. Edn., 1965, 4, 784.

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(liquid film).²³ This band may be ascribed to the carbonyl-stretching vibration in the *N*-plumbylcarbamate structure, but, as with the corresponding tin compounds,²³ the possibility of addition to the C=O group, and of intermolecular association of the adduct, cannot be excluded. Neumann and Kühlein reported a similar ambiguity in the structure of the plumbyltrialkylureas prepared from plumbylamides and isocyanates; ²¹ in the reaction of the lead hydrides with isocyanates, the initial addition was apparently obscured by subsequent reactions.²²

Di-1-naphthylcarbodi-imide similarly reacted rapidly with triphenyl-lead methoxide, to give the plumbylisourea (equation 10), which was monomeric in benzene. The C=N stretching frequency was at 1660 cm.⁻¹ (in Nujol), to be compared with the value of 1630 cm.⁻¹ (liquid film) in the corresponding tributylstannyl compound. Triphenyl-lead methoxide reacted exothermic-

$$\begin{array}{rl} \mbox{Ph}_{3}\mbox{Pb}\mbox{\cdot}O\mbox{Me} + 1\mbox{-}C_{10}\mbox{H}_{7}\mbox{\cdot}N=\mbox{C}_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{\cdot}N=\mbox{H}_{1}\mbox{-}C_{10}\mbox{H}_{7}\mbox{\cdot}N=\mbox{H}_{1}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{-}C_{10}\mbox{H}_{7}\mbox{-}C_{10}\mbox{-}C_{$$

ally with phenyl isothiocyanate, and the adduct could be isolated as a crystalline solid, stable to air.

$$Ph_{3}Pb OMe + PhNCS \longrightarrow Ph_{3}Pb S C (= NPh)OMe$$
 (11)

The product showed a band in the infrared spectrum at 1620 cm.⁻¹ (in Nujol), cf. 1625 cm.⁻¹ (liquid film) in the corresponding product from tributyltin methoxide, probably to be ascribed to the C=N stretching vibration, implying addition across the C=S bond as shown in equation (11).

Tributyl-lead methoxide similarly reacted exothermically with phenyl isothiocyanate, but the product decomposed almost immediately to give a black precipitate.

Similarly, carbon disulphide reacted readily with triphenyl-lead methoxide to give the stable dithiocarbonate, but tributyl-lead methoxide gave an unstable adduct from which only tetrabutyl-lead could be isolated.

Trichloroacetonitrile reacted exothermically with triphenyl-lead methoxide to give the crystalline N-plumbylimidate from which the parent imidate could be obtained by hydrolysis (equation 12).

$$Ph_{3}Pb \cdot OMe + N \equiv C \cdot CCI_{3} \longrightarrow Ph_{3}Pb \cdot N \equiv C(CCI_{3})OMe \xrightarrow{H_{2}O} HN \equiv C(CCI_{3})OMe \quad (12)$$

With acrylonitrile as the acceptor, 1,2-addition might occur at the C=N group, or at the C=C groups, or 1,4-addition might take place to give a ketenimine derivative. Triethyl-lead methoxide and acrylonitrile reacted exothermically, and the infrared and n.m.r. spectra showed that an equilibrium was established between the reactants (ca. 30%) and adduct (ca. 70%). The n.m.r. spectrum showed no signal below τ 6.2, and the infrared spectrum showed the presence of a C=N vibration at

²³ Part I, A. J. Bloodworth and A. G. Davies, J. Chem. Soc., 1965, 5238.

²⁴ G. Chandra, T. A. George, and M. F. Lappert, *Chem. Comm.*, 1967, 116.

2200 cm.⁻¹. 1,2-Addition therefore apparently occurs across the olefinic group, as shown in equation (13).

$Et_3Pb \cdot OMe + CH_2 = CH - C \equiv N \longrightarrow MeO \cdot CH_2 \cdot CH(PbEt_3)C \equiv N$ (13)

A similar mode of addition has been assumed in the reaction of triethyltin diethylamide with acrylonitrile,²⁴ but tributyl-lead hydride apparently adds in the opposite sense to give the adduct $Bu_3Pb\cdot CH_2\cdot CH_2\cdot C\equiv N.^{22}$

Triphenyl- and tributyl-lead methoxides both reacted with trichloroacetaldehyde (equation 14) to give 1:1adducts which were spectrally similar to those formed by tributyltin methoxide.²⁵

$$R_{3}Pb \cdot OMe + O=CH \cdot CCI_{3} \longrightarrow R_{3}Pb \cdot O \cdot CH(CCI_{3})OMe \longrightarrow R_{3}PbCI + O=CH \cdot OMe + [:CCI_{2}] (14)$$

The triphenyl-lead compound on melting gave triphenyl-lead chloride; the tributyl-lead derivative after 2 hr. at 90° gave an n.m.r. signal at $\tau 2.51$, apparently due to methyl formate, and the signal of the methine proton at 4.99 decayed.

The decomposition therefore follows the same course as that of the corresponding organotin adducts, suggesting that trihalogenomethyl-lead compounds might be prepared by the same method as the trihalogenomethyltins (equation 15).²⁶

$$M-OMe + O=CR-CX_{3} \longrightarrow M-O-C-OMe \longrightarrow CX_{3}$$

$$M-CX_{*} + O=C-OMe \quad (15)$$

Hexachloroacetone was treated with triphenyl-lead methoxide; an exothermic reaction took place (equation 15, $M = Ph_3Pb$, X = Cl, $R = Cl_3C$), and trichloromethyltriphenyl-lead was isolated as a crystalline solid, identical with the product obtained by treating the methoxide with chloroform. Similarly, tribromoacetaldehyde reacted with triphenyl-lead methoxide at room temperature (equation 15, $M = Ph_3Pb$, X = Br, R = H), to yield tribromomethyltriphenyl-lead, identical with the material obtained previously.

EXPERIMENTAL

General methods.—Infrared spectra of neat liquids or Nujol mulls of solids were recorded on a Unicam SP 200 or Perkin-Elmer 337 instrument. Proton magnetic resonance spectra were determined at 33° in carbon tetrachloride using a Perkin-Elmer R10 spectrometer.

The equivalent weights of organolead alkoxides were measured by titration of a known weight of the compound, dissolved in water, with standard hydrochloric acid, using Methyl Red indicator. Molecular weights were determined at 25° using a Mecrolab Vapour Pressure Osmometer, model 301A.

Thin-layer chromatography of organolead compounds was

²⁵ Part VI, A. G. Davies and W. R. Symes, *J. Chem. Soc.* (C), 1967, 1009.

²⁶ A. G. Davies and W. R. Symes, J. Organometallic Chem., 1966, **5**, 394. carried out on silica gel, using a 2% solution of dithizone in chloroform as the spray reagent. This gives a yellow spot with trialkyl-lead compounds, and a red spot with dialkyllead and inorganic lead compounds. Some $R_{\rm F}$ values are as follows (eluent, benzene); Oracet Orange 0.25, Ph₃PbCl 0.13, Ph₃Pb·CCl₃ 0.66, Ph₃PbBr 0.39, Ph₃Pb·CBr₃ 0.66, Bu₃PbCl 0.12, all R₂PbX₂ 0.00. Eluent, benzene-cyclohexane-acetic acid (6:3:1 by volume); Oracet Orange 0.43, Ph₂PbCl₂ 0.07, Bu₂PbCl₂ 0.06, Bu₂Pb(OAc)₂ 0.07.

Because of their toxicity, organolead compounds were always handled with rubber gloves, either in a glove box or in a well ventilated fume hood.

Organolead Reagents .--- Tetramethyl-lead and tetraethyllead were supplied by the Associated Octel Co. Ltd., and tributyl-lead chloride and triphenyl-lead chloride by the International Lead Zinc Research Organisation. methyl-lead bromide 15, 27 and triethyl-lead bromide 27 were prepared by treatment of the appropriate tetra-alkyl-lead in ether at -70° with bromine. Triethyl-lead hydroxide and trimethyl-lead hydroxide were obtained by shaking the corresponding methoxide in benzene with water, and then removing volatile material at the pump. Triethyl-lead hydroxide was alternatively obtained by treatment of triethyl-lead chloride with sodium hydroxide,28 and triphenyl-lead hydroxide and chloride by oxidation of hexaphenyldilead.15

Preparation of Trialkyl-lead Alkoxides.---One example of each of the three general methods is given in detail. Results of all the preparations are summarised in the Table. Trimethyl-lead isopropoxide and t-butoxide, and triethyl-lead benzyl oxide and 1-phenylethoxide were prepared by method (2) and trimethyl-lead 2,2-dimethylpropoxide by method (3) but these compounds could not be sublimed or distilled without decomposition.

(a) Triethyl-lead methoxide from triethyl-lead bromide and sodium methoxide. Triethyl-lead bromide (7.30 g., 19.6 mmoles) in dry ether (100 c.c.) was added to a solution of sodium methoxide [from sodium (0.522 g., 22.7 moles)] in methanol (5 c.c.). A precipitate of sodium bromide immediately separated. The mixture was stirred for 30 min., then centrifuged. The solvent was removed from the supernatant solution under reduced pressure, leaving a vellow oil (5.8 g.), which was sublimed at $60-80^{\circ}/0.01$ mm. to give triethyl-lead methoxide as a solid, m. p. 73-75°, in 71% yield.

(b) Trimethyl-lead proposide from trimethyl-lead methoside and propanol. A solution of trimethyl-lead methoxide (2.31 g., 8.19 mmoles) in propanol (50 c.c.) was distilled. The residue was sublimed at 70-100°/3 mm., to give trimethyl-lead propoxide as a solid, m. p. 129-131° (1.9 g., 57%).

(c) Triethyl-lead 2,2-dimethylpropoxide from triethyl-lead hydroxide and 2,2-dimethylpropanol. A solution of triethyllead hydroxide (2.36 g., 7.59 mmoles) and 2,2-dimethylpropanol (0.52 g., 7.59 mmoles) in benzene (25 c.c.) was heated under reflux in an apparatus fitted with a Dean and Stark water separator. The reaction was complete in 2 hr. The solvent was removed, and the residue was distilled, to yield triethyl-lead 2,2-dimethylproposide as a pale yellow liquid, b. p. 107-110°/0·1 mm., in 59% yield.

All the alkoxides were very easily hydrolysed in air; all were readily soluble in carbon tetrachloride and in benzene, but triphenyl-lead methoxide was sparingly soluble in ether, whereas, the trialkyl-lead alkoxides were soluble.

Freshly sublimed triethyl-lead methoxide in a sealed tube

reverted to an oily solid during a few weeks. In carbon tetrachloride, about 20% of tetra-ethyl-lead was formed in two weeks.

Reaction of Triethyl-lead Hydroxide with Dimethyl Carbonate.—A solution of triethyl-lead hydroxide (1.7 g., 5.2 mmoles) in dimethyl carbonate (10 c.c.) was heated under reflux for 1 hr. No evolution of carbon dioxide could be detected with lime water. A colourless solid precipitated, which was separated and extracted with boiling acetone (50 c.c.), to yield needles of bistriethyl-lead carbonate (0.9 g., 51%), m. p. $<300^{\circ},$ v_{max} (CO₃) 1521s, 1501s, 1055m, 845m, and 738m cm. $^{-1}$ (Found: C, 24.2; H, 4.8%; Equiv. wt., 324. C₁₃H₃₀O₃Pb₂ requires C, 24.1; H, 4.6%; Equiv. wt., 324).

Reaction of Triethyl-lead Methoxide with Phthalic Anhydride.--Triethyl-lead methoxide (0.88 g., 2.71 mmoles) was added to a suspension of phthalic anhydride (0.40 g., 2.71 mmoles) in benzene (5 c.c.). Heat was evolved, and a clear solution was obtained, which, on cooling, deposited crystals of methyl triethyl-lead phthalate (1.08 g., 84%), m. p. 119—120°, ν_{max} 1715 (C=O) cm.⁻¹ (Found: C, 38.6; H, 5.2%; M (in C₆H₆), 488. C₁₅H₂₂O₄Pb requires C, 38.1; H, 4.7%; M, 475).

Reaction of Triphenyl-lead Methoxide with Chloroform.-Triphenyl-lead methoxide (0.91 g., 1.94 mmoles) was dissolved in chloroform (10 c.c.); no heat was evolved. After 16 hr. the chloroform was removed under reduced pressure to leave a mixture of triphenyl-lead methoxide and trichloromethyltriphenyl-lead. This was dissolved in benzene (10 c.c.) and shaken with water (2 c.c.). The triphenyl-lead hydroxide (0.60 g., 68%) which was precipitated was filtered off. The solute was recovered from the benzene and was purified by chromatography in benzene over silica gel, yielding trichloromethyltriphenyl-lead (0.37 g., 34%), m. p. 169-170°; the m. p. was not depressed when the sample was mixed with the product obtained from the methoxide and hexachloroacetone.

Reaction of Triphenyl-lead Methoxide and Bromoform.-In a similar reaction, triphenyl-lead methoxide (1.25 g., 2.67 mmoles) and bromoform (10 c.c.) after 16 hr. yielded triphenyl-lead hydroxide (0.27 g., 22%) and tribromomethyltriphenyl-lead (1.28 g., 70%), m. p. 137-139°, identical with the product obtained from the methoxide and bromal (Found: Br, 32.9. Calc. for C₁₉H₁₅Br₃Pb: Br, 34.7%).

Reaction of Triethyl-lead Methoxide with Chloroform and with Bromoform.—These reactions were very exothermic, and therefore were carried out at low temperatures.

Triethyl-lead methoxide (1.20 g., 3.70 mmoles) and chloroform (5 c.c.) were mixed at -70° , and allowed to warm slowly to room temperature. After 2 hr., the excess of chloroform was removed under reduced pressure from the (now yellow) mixture, yielding a yellow oil which was readily hydrolysed in air. The n.m.r. spectrum showed that the product contained some 25% of unchanged methoxide.

In a similar process, triethyl-lead methoxide (1.10 g.) and bromoform (5 c.c.) yielded a yellow oily solid $[\nu_{\rm max},$ 600m and 656 cm.⁻¹ (CBr₃?)], which was readily hydrolysed in air, and contained no residual methoxide.

Reaction of Triethyl-lead Methoxide with Cyclopentadiene.-Freshly distilled cyclopentadiene (0.159 c.c., 1.84 mmoles) was added to a solution of triethyl-lead methoxide (0.63 g.)1.84 mmoles) in carbon tetrachloride (0.3 c.c.). The mixture

 G. Grüttner and E. Krause, Ber., 1916, 49, 1415.
 O. H. Brown and E. E. Reid, J. Amer. Chem. Soc., 1927, 49, 830.

immediately became yellow, and the n.m.r. spectrum showed that the reaction had gone to completion giving methanol, τ 6.50 (OMe) and 3.33 (OH), and cyclopentadienyltriethyllead τ 8.38 (singlet, C₂H₅) and 3.79 (C₅H₅). The reaction was repeated on the scale of 6.75 mmoles, and the product was isolated as a yellow oil which quickly turned brown: τ 8.31 and 3.81 [Fritz and Schwarzhans²⁹ report τ 8.44 (C_2H_5) ; 3.85 (C_5H_5) $J(Pb-C_5H_5) = 17$ c./sec.] In neither of our two samples was coupling apparent between the lead and the cyclopentadienyl protons.

Reaction of Organolead Alkoxides with Multiply Bonded Reagents.---(a) Isocyanates. (i) Heat was evolved when 1naphthyl isocyanate (0.49 c.c., 3.42 mmoles) was added to a solution of triphenyl-lead methoxide (1.60 g., 3.42 mmoles) in benzene (10 c.c.). The solvent was removed under reduced pressure, to yield methyl triphenylplumbyl-N-1naphthylcarbamate as a colourless solid which was washed with pentane and dried in vacuo (2.2 g., 100% yield), m. p. 135-141° (decomp.). In the solid state it was hydrolysed only slowly in air, but attempts to recrystallise it from benzene led to hydrolysis [Found: C, 57.9; H, 4.4; N, 2.4%; 1640 (C=O) cm.⁻¹; τ 6.32 (OMe).

A solution of the plumbylcarbamate (0.9 g.) in chloroform (10 c.c.) was shaken vigorously with water for 5 min. The triphenyl-lead hydroxide which was precipitated was filtered off, and the hydrolysis was repeated, giving methyl N-1-naphthylcarbamate (0.23 g.), which was recrystallised from chloroform; m. p. 123-124° (lit.23, m. p. 124°).

(ii) The reaction between tributyl-lead methoxide (0.46 g., 1.12 mmoles) and 1-naphthyl isocyanate (0.16 g., 1.12 mmoles) in carbon tetrachloride was similarly exothermic and gave methyl tributylplumbyl-N-1-naphthylcarbamate (0.62 g., 100%) as a colourless solid, m. p. 72-75°, which became dark brown when it was kept in a sealed tube for a few days; $\nu_{max.}$ 1640 (C=O) cm.^-1; τ 6.40 (OMe) [Found: C, 48.5; H, 6.6%; M (in C₆H₆), 565 (2.0%), 572 (3.3%), 603 (5.4%). Calc for C₂₄H₃₇NO₂Pb: C, 49.7; H, 6.4%; M, 578].

It was hydrolysed in the air more rapidly than the corresponding triphenylplumbylcarbamate. Hydrolysis carbon tetrachloride by the procedure above, gave methyl N-1-naphthylcarbamate, m. p. 119-123°.

(iii) Crude triethyl-lead 1-phenylethoxide (0.64 g., 1.54 mmole) reacted exothermically with phenyl isocyanate (0.168 c.c., 1.54 mmoles), to give a brown oil. This was hydrolysed in carbon tetrachloride, and the product was recrystallised from light petroleum, to yield 1-phenethyl N-phenylcarbamate, m. p. 93-94° (lit., m. p. 94°).

(b) Di-1-naphthylcarbodi-imide. Di-1-naphthylcarbodiimide (0.56 g., 1.90 mmoles) rapidly dissolved in a solution of triphenyl-lead methoxide (0.89 g., 1.90 mmoles) in benzene (20 c.c.), and the band at 2150 (N=C=N) in the infrared spectrum disappeared. The benzene was removed under reduced pressure, to yield NN'-di-1-naphthyl-N-triphenylplumbyl-O-methylisourea as a colourless solid (1.46 g., 100%), which was washed with pentane and dried; m. p. 120—140° (decomp.), v_{max} 1660 (C=N) cm.⁻¹; τ 5.85 (OMe) [Found: C, 63.6; H, 4.4; N, 3.9%; M (in C₆H₆), 726 (1.2%), 733 (1.9%). Calc. for $C_{40}H_{32}N_2OPb$: C, 62.8; H, 4.2; N, 3.7%; M, 764].

(c) Phenyl isothiocyanate. (i) Heat was evolved when phenyl isothiocyanate (0.56 c.c., 4.73 mmoles) was added to a solution of triphenyl-lead methoxide (2.22 g., 4.73

mmoles) in benzene (20 c.c.). The benzene was removed under reduced pressure, to yield O-methyl-S-triphenylplumbyl-N-phenylthiocarbimidate which recrystallised as needles from benzene-light petroleum (2.08 g., 72%), m. p. 107—120° (decomp.), v_{max} 1620vs (C=N) cm.⁻¹; τ 6·36 (OMe) [Found: C, 51·6; H, 4·0; N, 2·2%; M (in C₆H₆), 570 (2.0%), 573 (2.3%). $C_{26}H_{23}NOPbS$ requires C, 51.5; H, 3.8; N, 2.3%; M, 604].

(ii) The reaction between phenyl isothiocyanate (0.17 c.c.) and tributyl-lead methoxide (0.58 g.) in carbon tetrachloride was similarly exothermic, but a black precipitate, apparently of lead sulphide, appeared almost immediately.

(d) Carbon disulphide. (i) Carbon disulphide (0.20 g., 2.62 mmoles) was added to a solution of triphenyl-lead methoxide (1.08 g, 2.31 mmoles) in benzene (15 c.c.). The benzene was removed under reduced pressure, to leave a colourless solid, which was washed with pentane and recrystallised from ether, to yield O-methyl-S-triphenyl-lead dithiocarbamate (1.07 g., 85%); τ 6.11 (OMe) [Found: C, 45.5; H, 3.5%; M (in C_6H_6), 560 (1.0%), 566 (1.3%), 584 (2.9%), 601 (5.7%). Calc. for $C_{20}H_{18}OPbS_2$: C, 44.0, H, 3·3%; M, 545.]

(ii) A black precipitate appeared almost immediately when equivalent amounts of tributyl-lead methoxide and carbon disulphide were mixed in carbon tetrachloride. When the solvent was removed, a black solid suspended in a colourless oil remained, but distillation of this gave only tetrabutyl-lead.

(e) Carbon dioxide. (i) Dry carbon dioxide was passed through a solution of triethyl-lead methoxide (0.65 g.) in dry ether (15 c.c.). The solution was filtered and the solvent was removed under reduced pressure to leave methyl triethyl-lead carbonate as a white solid (0.62 g.)84%), m. p. 60—62°, ν_{max} 1625vs (C=O) cm.⁻¹, 1090s (C=O) cm.⁻¹; τ 6·39 (OMe) (cf. 1600 and 1095 cm.⁻¹ for Bu₃Sn·O·CO·OMe ⁶) (Found: C, 25·4; H, 4·5%; Equiv. wt., 373. C₈H₁₈O₃Pb requires C, 26·1; H, 4·9%; Equiv. wt., 369).

(ii) Tri-p-tolyl-lead hydroxide (2.8 g.) dissolved rapidly in benzene (10 c.c.) when carbon dioxide was passed through the suspension. After 15 min. the solvent was removed, to yield bis(tri-p-tolyl-lead)carbonate (2.9 g.), decomp. 90-100°, 7 7.70 (Me) (Found: C, 50.9; H, 4.1: C43H42O3Pb2 requires C, 50.6; H, 4.1%).

(f) Trichloroacetonitrile.—Trichloroacetonitrile (0.23 g., 1.60 mmoles) was added to a solution of triphenyl-lead methoxide (0.75 g., 1.60 mmoles) in benzene (15 c.c.); heat was evolved. The solvent was removed under reduced pressure, to leave O-methyl-N-triphenylplumbyltrichloroacetimidate (0.98 g., 100%), which was washed with pentane and dried, m. p. 127–131°, ν_{max} 1665 (C=N) cm.⁻¹, τ (in C, 40.9; H, 3.0. 5.96(OMe) [Found: Me₂CO) $C_{21}H_{18}Cl_3NOPb$ requires C, 40.8; H, 2.9%]. It was too insoluble for the molecular weight to be determined.

A suspension of the above plumbylimidate (0.78 g.) in carbon tetrachloride (10 c.c.) was boiled with water (1 c.c.) for 5 min., to yield triphenyl-lead hydroxide which was filtered off, and O-methyltrichloroacetimidate with an infrared and n.m.r. spectrum identical with those of the authentic material.30

(g) Acrylonitrile. Acrylonitrile (0.084 c.c., 1.23 mmoles) was added to a solution of triethyl-lead methoxide (0.40 g.,

29 H. P. Fritz and K. E. Schwarzhans, J. Organometallic Chem., 1964, 1, 297. ³⁰ W. Steinkopf, Ber., 1907, 40, 1643.

1.23 mmole) in carbon tetrachloride. An exothermic reaction took place and the solution became yellow-brown. The integrated n.m.r. spectrum showed that about 30% of the acrylonitrile was unchanged, and that a product had been formed, probably of the structure MeO·CH₂·CH(C=N)PbEt₃ [τ , triplets at 7.34 (CH) $J(CH_2\cdotCH) = 6.6$ c./sec.; the signals for the CH₂ group and for the methoxy-groups in the reactant and product were not resolved between τ 6.2 and 6.7.] The spectrum of the acrylonitrile persisted when an excess of triethyl-lead methoxide was added, showing that the reaction was an equilibrium.

The reaction was repeated with triethyl-lead methoxide (0.17 g.) and acrylonitrile (0.034 c.c.) in carbon tetrachloride (1.0 c.c.). The infrared spectrum showed weak bands due to the free nitrile at 2230, 1655, and 1615 cm.⁻¹, and a band at 2200 cm.⁻¹ which may be ascribed to the C=N group in the adduct. Methanolysis of the product gave β -methoxy-propionitrile, identical with the authentic material.³¹

(h) Trichloroacetaldehyde. (i) Heat was evolved when trichloroacetaldehyde (0.49 c.c., 5.04 mmoles) was added to a solution of triphenyl-lead methoxide (2.36 g., 5.04 mmoles) in benzene. The solvent was removed under reduced pressure leaving 1,1,1-trichloro-2-methoxy-2-triphenylplumbyl-oxyethane as a colourless solid, which was washed with pentane (3.1 g., 100%), m. p. 96—100° with effervescence, then resolidifying; τ 6.63 (OMe), 4.78 (Cl₃C·CH) (cf. τ 6.43 and 5.05 in the corresponding adduct of tributyltin methoxide ²⁵) (Found: C, 41.9; H, 3.3%; M (in C₆H₆), 659 (1.4%), 698 (3.2%). Calc. for C₂₁H₁₉Cl₃O₂Pb: C, 40.8; H, 3.1%; M, 617). The solid recovered after melting had taken place was recrystallised from benzene, and identified as triphenyl-lead chloride, m. p. 205—207° (lit⁷, m. p. 210°).

(ii) Tributyl-lead methoxide (0.83 g., 2.03 mmoles) reacted with chloral (0.20 c.c., 2.03 mmoles) in carbon tetrachloride (10 c.c.) to give the adduct as a yellow oil which was not purified; τ 6.38 (OMe), 4.99 (Cl₃C·CH).

³¹ J. H. McGregor and C. Pugh, J. Chem. Soc., 1945, 535.

The sample was kept at 90° for 2 hr.; the signal at τ 4.99 disappeared, and a new one at 2.51 appeared, probably due to the formation of methyl formate.

(i) Hexachloroacetone. Hexachloroacetone (0.28 c.c., 1.84 mmoles) was added to a solution of triphenyl-lead methoxide (0.86 g., 1.84 mmoles) in benzene (20 c.c.); heat was evolved, and the mixture was cooled in ice. After a few minutes, the benzene was removed under reduced pressure, to yield a colourless solid (0.99 g.), m. p. 165° (decomp.), which, by potentiometric titration for chloride and by thin-layer chromatography, was found to consist of a mixture of 40%of Ph₃PbCl and 60% of Ph₃PbCCl₃. The components (0.50 g. scale) were separated by chromatography in benzene over a column of silica gel, to yield trichloromethyltriphenyl-lead (0.15 g., 30%), m. p. 171-171.5°, resolidifying (Found: C, 41.4; H, 3.0; Cl, 18.9%; M (in C₆H₆), 551. C₁₉H₁₅Cl₃Pb requires C, 40.9; H, 2.7; Cl, 19.1%; M, 556). It reacted with aniline and alkali to give the odour of phenyl isocyanide.

(j) Tribromoacetaldehyde. Bromal (0·27 c.c., 2·77 mmoles) was added to a solution of triphenyl-lead methoxide (1·30 g., 2·77 mmoles) in benzene (20 c.c.); little heat was evolved. The solvent was removed under reduced pressure to yield a pale brown solid, which was shown by t.l.c. to consist of a mixture of Ph₃PbBr and Ph₃Pb·CBr₃. A sample of the mixture (0·50 g.) was fractionated chromatographically as above, to yield tribromomethyltriphenyl-lead (0·16 g., 32%), as a colourless solid, m. p. 135—140° (turning yellow), v_{max} . 615 (C–Br) cm.⁻¹ (Found: C, 34·4; H, 2·6; Br, 33·8%, M (in Me₂CO), 662. Calc. for C₁₉H₁₅Br₃Pb: C, 33·1; H, 2·2; Br, 34·7%; M, 690).

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