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ACETOLYSIS OF HEXAARYLDILEADS

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SUMMARY

The acetolyses of hexaaryldileads, $(XC_6H_4)_6Pb_2$ in which X is H, *p*-CH_3O, *m*- and *p*-CH_3, *m*- and *p*-Cl and 2,5-$(CH_3)_2$, have been examined kinetically at 40° in 1/3 acetic acid/dioxane solution. Hexaphenyldilead has been examined also at several temperatures, in two other acetic acid/dioxane solutions and in the presence of various added salts and tetraphenyllead. The results are not consistent with a prior dissociation to tetraaryllead and diaryllead, but correspond to electrophilic C–Pb cleavage to yield a partially acetoxylated derivative which decomposes to the observed products triaryllead acetate, diaryllead diacetate, lead(II) acetate and aromatic hydrocarbon.

Partially acetoxylated derivatives, $Ar_3Pb_2(OCOCH_3)_3$ where Ar is phenyl and *p*-tolyl, have been prepared in acetic anhydride/acetic acid solution and on the basis of mass spectra are suggested to possess the unsymmetrical $(CH_3COO)Ar_2PbPbAr(OCOCH_3)_2$ structures.

Employing ^{14}C labelled materials it has been found that no detectable exchange takes place between hexaphenyldilead and tetraphenyllead in benzene or tetrahydrofuran solution at 40°, nor between hexaphenyldilead and triphenyllead chloride in benzene solution at 40°.

INTRODUCTION

Several stoichiometric studies have shown that in the protolysis of hexaalkyl and hexaaryldileads both Pb–C and Pb–Pb bond cleavage takes place. Hydrogen chloride in chloroform[1,2] converts the alkyl derivatives to trialkyllead chlorides according to eqn. (1).

$$R_6Pb_2 + 3\ HCl \rightarrow R_3PbCl + PbCl_2 + 3\ RH \qquad (1)$$

while the aryl derivatives[2-5] follow eqn. (2),

$$Ar_6Pb_2 + 4\ HCl \rightarrow Ar_2PbCl_2 + PbCl_2 + 4\ RH \qquad (2)$$

as a result of the greater reactivity of the triaryllead chlorides towards acid. Separate experiments demonstrated that lead(II) chloride does not arise from the R_3PbCl species, nor from the R_4Pb species, which under these conditions yields R_3PbCl or Ar_2PbCl_2.

However, hydrogen chloride in methanol solution, generated by the methanolysis of acyl chlorides, is reported to convert hexaethyldilead to tetraethyllead or triethyllead chloride[6], *i.e.*

$$(C_2H_5)_6Pb_2+2\,HCl \longrightarrow (C_2H_5)_4Pb+PbCl_2+2\,C_2H_6$$

$$\xrightarrow{HCl} (C_2H_5)_3PbCl \qquad (3)$$

and the product of acetic acid reaction of hexaphenyldilead in refluxing benzene solution[7], contains tetraphenyllead as a dominant product.

$$(C_6H_5)_6Pb_2+2\,CH_3CO_2H \rightarrow$$

$$\underset{25\%}{2\,C_6H_6}+\underset{41\%}{(C_6H_5)_4Pb}+Pb(OCOCH_3)_2+\underset{18\%}{(C_6H_5)_3PbOCOCH_3} \qquad (4)$$

To account for the results expressed in eqns. (3) and (4) it has been suggested that dissociation takes place, thus:

$$R_6Pb_2 \rightleftharpoons R_4Pb+R_2Pb \qquad (5)$$

and that the products arise from the extremely reactive dialkyllead and the less reactive tetraalkyllead. In support of this suggestion is the report[8] that hexaphenyldilead labelled with radio-active lead undergoes rapid exchange with tetraphenyllead in benzene solution at 40°. This equilibrium has been employed to account for a number of reactions of dilead derivatives[9].

However, when hexaphenyldilead and hydrogen chloride are reacted in 1/1 ratio at low temperature no tetraphenyllead is detected in the product[10]. Triphenyllead chloride, lead(II) chloride and unchanged substrate are obtained. Furthermore tetraphenyllead is formed in the thermal decomposition of hexaphenyllead that takes place for example on refluxing in benzene solution[4] (*cf*. ref. 7).

The validity of eqn. (5) as an *equilibrium* as opposed to a mode of decomposition has also been questioned[10] on the grounds that hexaphenyldilead does not show the hydrolytic instability expected if diphenyllead were formed from it, and that preparations believed to be diphenyllead do not react with tetraphenyllead in the reverse of eqn. (5).

The present studies were carried out to clarify the mechanism of protolysis of hexaaryldileads and to examine the status of reaction (5).

EXPERIMENTAL

1. *Materials*

Hexaphenyldilead, hexa-*p*-tolyldilead and tetraphenyllead were obtained from the International Lead Zinc Research Organization through Dr. G. M. van der Want, Organisch Chemisch Instituut TNO, Utrecht.

Hexakis(*p*-methoxyphenyl)dilead, prepared according to the method of Gilman and Towne[5] in 55–60% yield, had a decomposition point of 196° (reported 198–200°). (Found: C, 47.70; H, 3.97. $C_{42}H_{42}O_6Pb_2$ calcd.: C, 47.72; H, 3.97%.)

Hexa-*m*-tolyldilead, prepared according to the method of Gilman and

Bailie[4], had m.p. 107° (reported 109°). (Found: C, 52.56; H, 4.40. $C_{42}H_{42}Pb_2$ calcd.: C, 52.50; H, 4.37%.)

Hexakis(*m*-chlorophenyl)dilead, prepared by the Gilman–Bailie method[4] from *m*-bromochlorobenzene in 41% yield, was crystallised from chloroform after the crude product had been washed with cold ethanol. The cream coloured crystals had a decomposition point of 121–123°. (Found: C, 39.91; H, 2.18. $C_{36}H_{24}Cl_6Pb_2$ calcd.: C, 39.88; H, 2.21%.) Short Grignard reaction times were required to minimise the formation of tetrakis(*m*-chlorophenyl)lead. Subsequent investigations suggest that alcoholysis of hexaaryldileads containing electron-withdrawing substituents reduces the yield of product and hence the effectiveness of alcohol washing during purification.

Hexakis(*p*-chlorophenyl)dilead was prepared similarly from *p*-chlorobromobenzene in 35–45% yield as cream coloured crystals from chloroform decomposing at 185°. (Found: C, 39.85; H, 2.23. $C_{36}H_{24}Cl_6Pb_2$ calcd.: C, 39.88; H, 2.21%.)

Hexaphenyldilead and tetraphenyllead labelled with ^{14}C were prepared from bromobenzene having a specific activity of 0.157 millicuries/mole by the Gilman–Bailie[4] and Willemsens–Van der Kerk[10] methods respectively.

Dioxane was purified by the procedure of Vogel[11], peroxides being removed by passage through a column of activated alumina under a nitrogen atmosphere.

Acetic acid was purified by the method of Eichelberger and La Mer[12]. Karl Fischer estimation showed a water content of less than 10^{-3} *M*.

Propionic acid was dried over anhydrous sodium sulphate and fractionally distilled. The fraction in the 139–141° range was refractionated over potassium permanganate and the middle fraction distilling at 140.7° was employed.

The salts employed were all A.R. grade chemicals.

2. *Kinetic measurements*

A calculated amount of the hexaaryldilead was dissolved in dioxane so that on addition of the requisite amount of acetic acid a solution ca. 5×10^{-5} *M* was obtained. The concentration change was followed by observation at the previously determined λ_{max} value associated with the dilead system, (see Table 5), at which there is negligible absorption by the tetraaryllead, the solvent system and any additives. (Molar extinction coefficients for all compounds are in the range 30,000–34,000 as determined by extrapolation of the log absorption time curves to zero time.) A Cary-14 recording spectrophotometer equipped with a high intensity light source and thermostatted cell compartment was employed. The temperature variations were within ±0.1° for the 30° and 40° runs and within ±0.2° for the 50° runs.

A dual compartment reaction flask containing respectively the dioxane solution and the acetic acid components was pre-heated to the required temperature in a thermostatted bath, the components were rapidly mixed and a sample poured into the spectrophotometer cell (1 cm path length, quartz). The mixing and transfer operations were carried out in ca. 30 sec. First order rate constants were obtained from linear logarithm absorbance-to-time plots the reactions being followed to 60–80% completion.

3. *Product examination*

The stoichiometry of the acetolysis, the product composition during reaction, and the possible presence of intermediates were investigated by means of thin-layer chromatography. Glass plates (20 × 10 cm) were employed. These were cleaned by treatment with fresh chromic acid and scrubbing with steel wool in the presence of detergent. The clean dried plates were coated to 0.5 mm thickness with silica gel G and activated by heating for one hour at ca. 150°.

Two solvent systems were employed. Benzene/n-hexane (1/4 v/v) caused no migration of triaryllead acetates, diaryllead diacetates nor lead(II) acetate, while hexaaryldileads and tetraaryleads were clearly resolved the latter having the higher R_f value. With benzene/methanol (5/1 v/v) lead(II) acetate remains essentially static while the other species present become distinguishable.

Both 0.1 *N* aqueous potassium permanganate and dithizone in chloroform sprays were used. The former yields yellow spots on a pink background; and the latter gives yellow or orange spots on a green-blue background.

4. *Exchange studies*

Hexaphenyldilead (1 g) and tetraphenyllead (0.59 g), one of which was enriched in ^{14}C, were separately dissolved in benzene or tetrahydrofuran and placed in a thermostatted bath at 40°. The solutions were mixed and after the appropriate time interval (5 min, 75 min or 48 h) poured into less than an equal volume of cold ethanol. Most of the tetraphenyllead was precipitated and subsequently recrystallised from chloroform. Evaporation of the filtrate, followed by precipitation from chloroform solution by means of ethanol yielded the hexaphenyldilead. The purity of the recovered materials was assessed by thin-layer chromatography.

Counting was performed with a Chicago Nuclear Mark I Liquid Scintillation Counter with samples ca. 7×10^{-4} *M*. The scintillating liquid employed was toluene containing 2,5-diphenyloxazole (4 g/l) and *p*-bis(5-phenyl-2-oxazolyl)benzene (50 mg/l). Counts were corrected for counting efficiency (70–80%).

5. *Partially acetoxylated compounds*

Triphenyldilead triacetate was prepared from hexaphenyldilead (2 g) by reaction with acetic acid (15 ml) and acetic anhydride (2 ml) by heating under reflux in a nitrogen atmosphere for ca. 19 h. The colourless solution became yellow and finally dark brown. The syrupy liquid was triturated with 1/1 ether/acetone until a white crystalline mass was obtained. Residual hexaphenyldilead was removed by washing with chloroform and the air-dried product was sublimed at 140° under 0.1 mm pressure. White crystals decomposing sharply at 187–188° were obtained. (Found: C, 35.71; H, 3.18. $C_{24}H_{24}O_6Pb_2$ calcd.: C, 35.03; H, 2.92%.) The product is soluble in dichloromethane and slightly in chloroform. The PMR spectrum (CH_2Cl_2) shows a symmetrical multiplet at τ 2.45 (phenyl group) and a singlet at τ 8.02 (acetate methyl) with intensity ratios 5/3. A very strong, broad band in the IR spectrum is centred at 1535 cm^{-1} (acetate carbonyl group). There is no UV absorption in the 290–300 mμ region. A search for a Pb–Pb stretching frequency in the Raman spectrum of the solid was precluded by a considerable fluorescence.

The mass spectra were obtained using an Atlas CH4 with TO4 ion source. Lead containing ions were identified by the isotopic compositions:

Pb	208/207/206/204 ≃ 100/40/51/3
Pb_2	416/415/414/413/412/411 ≃ 85/68.5/100/35/26.5/2/2

The main ions observed at $m/e > 200$ and intensities not less than ca. 0.5% of the main peak are listed in Table 7 in terms of Pb (208) and Pb_2 (414) excluding the remainder of each isotopic pattern. The corresponding main ion spectrum for hexaphenyldilead is given in Table 8.

Tri-*p*-tolyldilead triacetate prepared similarly decomposed sharply at 191–192°. (Found: C, 36.92: H, 3.41. $C_{27}H_{30}O_6Pb_2$ calcd.: C, 37.50; H, 3.47%.) The PMR spectrum (CH_2Cl_2) showed a quartet at τ 2.60 (aromatics) and singlets at τ 7.64 (*p*-tolyl methyl) and τ 8.08 (acetate methyl) with intensity ratios 4/3/3. The strong, broad band in the IR spectrum is centred at 1520 cm^{-1}, and there is no UV absorption in the 290–300 $m\mu$ region.

The main ions observed in the mass spectrum are given in Table 9.

RESULTS

Thin-layer chromatographic examination of the acetolysis reaction mixture during reaction shows that only triaryllead acetate, diaryllead diacetate, lead(II) acetate and hexaaryldilead are present. Furthermore spot densities indicate that diaryllead diacetate is formed at the expense of triaryllead acetate. Tetraaryllead and lead(IV) acetate could not be detected at any stage. First order acetolysis rate constants (k_{obs}) are given in Table 1 for three acetic acid/dioxane media. The reproducibility of the rate constant under the most frequently employed conditions is also indicated (see also Table 5).

TABLE 1

ACETOLYSIS OF $(C_6H_5)_6Pb_2$ AT 40.0±0.1°

Medium	k^a_{obs} (sec^{-1})
1/3 (v/v) acetic acid/dioxane (4.36 *M* acetic acid)	5.85×10^{-5} 5.79×10^{-5}
1/1 (v/v) acetic acid/dioxane (8.71 *M* acetic acid)	4.55×10^{-4}
3/1 (v/v) acetic acid/dioxane (13.12 *M* acetic acid)	1.97×10^{-3}

[a] Observed first order rate constants.

No integral order in acetic acid could be found, although the data can be fitted to,

$$k_{obs} = 2.5 \times 10^{-6} [CH_3CO_2H]^{3.4} sec^{-1}$$

The dielectric constants of the pure components are dioxane (2.21) and acetic acid (6.19) at 25°, so that the weighted mean value changes from 3.2 to 4.2 to 5.2 as the acetic acid concentration changes from 4.36 to 8.71 to 13.12 *M*. The absence of a detectable salt effect, see Table 3, argues against an important dielectric effect.

Table 2 summarises the variation of rate with temperature from which

$$k_{obs} = 8.8 \times 10^6 \times \exp[-16 \text{ kcal} \cdot \text{mole}^{-1}/(R \cdot T)] \text{ sec}^{-1}$$

was obtained from the linear relationship between log k_{obs} and the reciprocal absolute temperature.

Various added salts and added tetraphenyllead are seen from Table 3 to have

TABLE 2

ACETOLYSIS OF $(C_6H_5)_6Pb_2$ IN 1/3 ACETIC ACID/DIOXANE

Temp (°C)	k_{obs}		
30.0±0.1°	2.46×10^{-5} sec^{-1}	Log A	$= 6.95$
40.0±0.1°	5.79×10^{-5} sec^{-1}	$\therefore A$	$= 8.8 \times 10^6$ sec^{-1}
40.8±0.1°	6.30×10^{-5} sec^{-1}	E_{act}	$= 16$ kcal·mole^{-1}
50.0±0.2°	12.32×10^{-5} sec^{-1}	$\therefore \Delta H^{\neq}$	$= 15.5$ kcal·mole^{-1}

TABLE 3

ACETOLYSIS OF $(C_6H_5)_6Pb_2$ IN 1/3 ACETIC ACID/DIOXANE

Added salts etc.	Temp. (°C)	$k_{obs}(10^{-5}$ sec)
None	40.0	5.82
$NaOCOCH_3$ (1.03 M)	40.0	5.88
$NaOCOCH_3$ (1.55 M)	40.0	5.90
$KClO_4$ (0.82 M)	40.0	5.90
$(C_6H_5)_4Pb$ (0.22 M)	40.0	5.86
$(C_6H_5)_4Pb$ (0.815 M)	40.0	5.72
None	40.8	6.30
KCl (1.61 M)	40.8	6.35
$KClO_4$ (0.505 M)	40.8	6.35

no significant effect upon the rate constant. Furthermore the slower acetolysis rate for tetraphenyllead results in the recovery of most of this additive when the acetolysis of hexaphenyldilead is essentially complete.

Table 4 shows that for both hexaphenyl and hexa-*p*-tolyldilead acetic acid is about three times more reactive than propionic acid. In aqueous solution at 25° acetic acid is the stronger by a factor of 1.3. Reaction with trifluoroacetic acid was too fast to be accurately followed under comparable conditions, while added perchloric acid is very rapidly consumed in a fast acidolysis which is followed by the normal acetolysis of residual substrate.

TABLE 4

SOLVOLYSIS OF $(C_6H_5)_6Pb_2$ AND $(p\text{-}CH_3C_6H_4)_6Pb_2$ IN 1/3 PROPIONIC ACID/DIOXANE

Substrate	Medium	k_{obs} (sec^{-1}) at 40°	k_{AC}/k_{PR}
$(C_6H_5)_6Pb_2$	1/3 propionic acid/dioxane	2.08×10^{-5}	2.8
	1/3 acetic acid/dioxane	5.85×10^{-5}	
$(p\text{-}CH_3C_6H_4)_6Pb_2$	1/3 propionic acid/dioxane	1.10×10^{-4}	3.1
	1/3 acetic acid/dioxane	3.43×10^{-4}	

The nature of the substituent in hexaaryldileads has a marked effect upon the acetolysis rate as shown in Table 5. The variation of log k_{obs} with the normal σ-values is not linear due to a pronounced rate enhancement by electron releasing groups. Linearity is achieved by the use of σ^+ values for the deviating members as illustrated in Fig. 1 from which a ρ^+ value of -2.3 is obtained.

TABLE 5

ACETOLYSIS OF $(XC_6H_4)_6Pb_2$ IN 1/3 ACETIC ACID/DIOXANE AT 40.0°

X	$\lambda_{max}(\mu)$	σ^a	$(\sigma^+)^a$	k_{obs} (sec^{-1})
p-CH_3O	302.3	−0.11	(−0.80)	$4.48(\pm 0.03) \times 10^{-3}$
p-CH_3	297.0	−0.13	(−0.32)	$3.43(\pm 0.02) \times 10^{-4}$
m-CH_3	299.4	−0.07		$1.16(\pm 0.01) \times 10^{-4}$
H	293.0	0.00		$5.82(\pm 0.03) \times 10^{-5}$
p-Cl	299.0	0.24	(0.11)	$2.63(\pm 0.02) \times 10^{-5}$
m-Cl	301.0	0.37		$1.07(\pm 0.01) \times 10^{-5}$
2,5-$(CH_3)_2$	307.6	—		$6.0\ (\pm 0.05) \times 10^{-6}$

[a] From ref. 13.

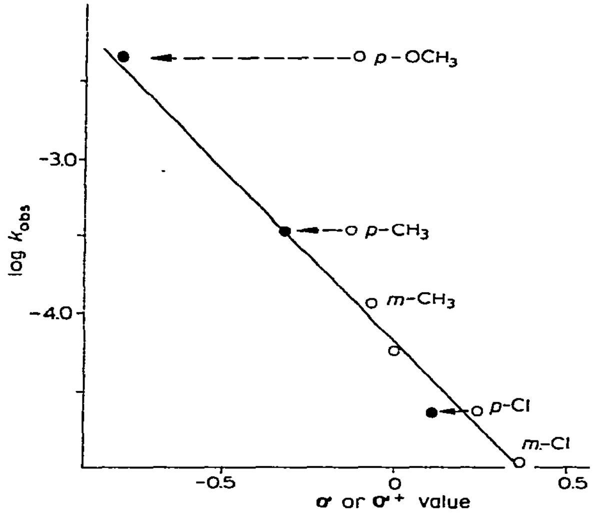


Fig. 1. Correlation of log k_{obs} with σ (open circles) or σ^+ (closed circles).

TABLE 6

PHENYL GROUP EXCHANGE STUDIES AT 40°

System	Counts per minute				Solvent
	Initial	5 min	75 min	48 h	
$Ph_6^*Pb_2$	6812	6680	6544		Benzene
$+Ph_4Pb$	0^a	78	43		
Ph_6Pb_2	0^a			42	Benzene
$+Ph_4^*Pb$	4567			4431	
$Ph_6^*Pb_2$	6812	6825	6577		Tetrahydrofuran
$+Ph_4Pb$	0^a	67	79		
$Ph_6^*Pb_2$	6812		6609		Benzene
$+Ph_3PbCl$	0^a		81		

[a] Background count not included.

Bearing in mind counting errors and a little ineffectiveness in the separation of hexaphenyldilead and tetraphenyllead, the results given in Table 6 show that no significant exchange of phenyl groups takes place between these species nor between hexaphenyldilead and triphenyllead chloride under the conditions examined.

DISCUSSION

The acetolysis reaction appears to follow the overall scheme of essentially irreversible reactions (6) and (7).

$$Ar_6Pb_2 + 3\,CH_3CO_2H \rightarrow Ar_3PbOCOCH_3 + Pb(OCOCH_3)_2 + 3\,ArH \quad (6)$$

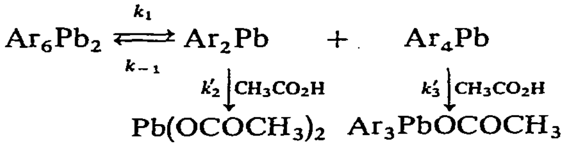
$$Ar_3PbOCOCH_3 + CH_3CO_2H \rightarrow Ar_2Pb(OCOCH_3)_2 + ArH \quad (7)$$

with no detectable side reactions. The rate of reaction as determined by the disappearance of the dilead species:

$$-d[Ar_6Pb_2]/dt = k_{obs} \cdot [Ar_6Pb_2] \quad (8)$$

refers therefore only to the rate controlling step of reaction (6), which is unimolecular in hexaaryldilead and has some indeterminate, possibly high order dependence on acetic acid. Reaction (7) may follow a little more slowly than reaction (6) but would not be observed kinetically.

A mechanism involving an equilibrium dissociation followed by rapid reaction of a diaryllead intermediate thus,



$$\begin{tikzcd} Ar_6Pb_2 \arrow[r, shift left, "k_1"] & Ar_2Pb \arrow[l, shift left, "k_{-1}"] \arrow[d, "k'_2\ CH_3CO_2H"] & + & Ar_4Pb \arrow[d, "k'_3\ CH_3CO_2H"] \\ & Pb(OCOCH_3)_2 & & Ar_3PbOCOCH_3 \end{tikzcd} \quad (9)$$

would lead to an observed rate constant,

$$k_{obs} = k_1 \left(1 + \frac{k_{-1} \cdot [Ar_4Pb]}{k'_2} \right)^{-1} \quad (10)$$

The results given in Table 3 indicate that within experimental error k_{obs} is independent of $[(C_6H_5)_4Pb]$, but taking the most optimistic view of the result for the 0.815 *M* addition one may have $k_{-1} \simeq 2 \times 10^{-2}\, k'_2$. This implies not only a quite rapid reversal of the dissociation, which our exchange studies do not substantiate, but also, since $k'_3 < k_{obs} \simeq k_1 < k'_2$, that there is no means by which a build-up of tetraphenyllead in the reaction mixture could be prevented.

$$d[(C_6H_5)_4Pb]/dt = k_1 \cdot [(C_6H_5)_4Pb] - [(C_6H_5)_4Pb] \cdot \left\{ k'_3 + \frac{k_1 \cdot k_{-1}}{k'_2} [(C_6H_5)_6Pb_2] \right\} \quad (11)$$

If the dissociation were essentially irreversible, $k_{-1} \ll k_1$, k'_2 and k'_3, the formation of tetraphenyllead would be even more evident.

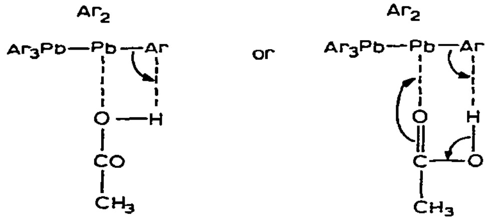
It seems most unlikely that the mechanism involves electrophilic Pb–Pb bond cleavage in the sense of eqn. (12):

$$Ar_6Pb_2 + CH_3CO_2H \rightarrow Ar_3PbOCOCH_3 + Ar_3PbH \quad (12)$$

since the most probable subsequent reaction of the hydride would be,

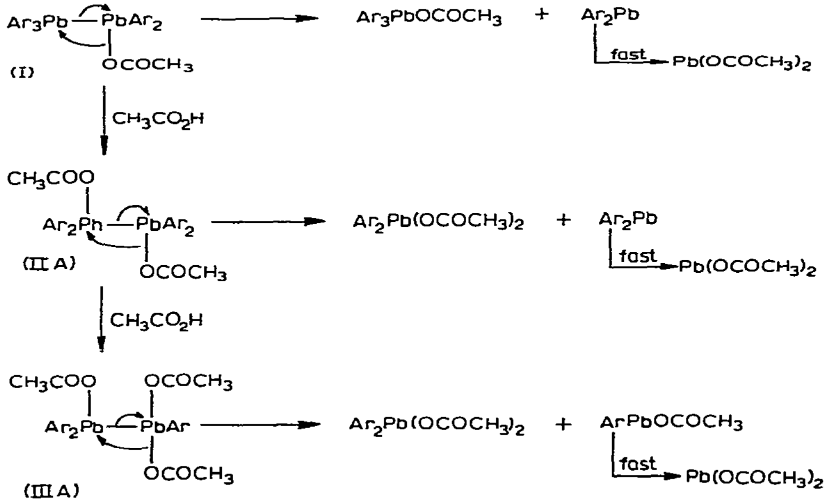
$$Ar_3PbH+CH_3CO_2H \rightarrow Ar_3PbOCOCH_3+H_2 \quad (13)$$

But the strongest evidence in favour of electrophilic Pb–C bond cleavage is the substituent dependence and the ρ^+ value, -2.3, is comparable with that for the hydrogen chloride reaction of diaryl mercurials[14], -2.8, and is consistent with proton attack at carbon concerted with acetate attack at lead in a four-centre transition state which is rather insensitive to the surrounding medium, *i.e.*



(14)

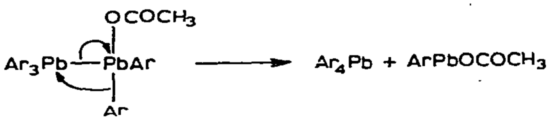
This partially acetoxylated intermediate may suffer further Pb–Pb bond cleavage in the manner suggested[2,10] for the hydrogen chloride reactions thus,



(15)

and give rise to the acetolysis products by the decompositions indicated in eqn. (15). Diaryllead diacetate is then formed at the expense of triaryllead acetate although not directly from it. Intermediates (IIA) and (IIIA) are preferred to their isomers, $Ar_3PbPbAr(OCOCH_3)_2$ (IIB) and $Ar_3PbPb(OCOCH_3)_3$ (IIIB), in view of the effect the acetoxy group in (I) would have upon the reactivity of an aryl group bonded to the same lead atom.

A competing reaction, (16), which may set in at higher temperatures, *e.g.* refluxing benzene, could account for tetraaryllead formation[7], although we do not observe this reaction even at 50°.



(16)

Little can be said at present about these postulated intermediates and their breakdown patterns since until the present investigations compounds of the type $R_nPb_2X_{6-n}$ were unknown. Following a procedure similar to that employed for the conversion of ditin derivatives to $Sn_2(OCOCH_3)_6$[15] we have succeeded in preparing $Ar_3Pb_2(OCOCH_3)_3$ in which Ar is phenyl and *p*-tolyl. Although only one type of acetate and one type of aryl group is observed in the PMR spectrum, we nevertheless prefer the formulation of the products as (IIIA) and not the more symmetrical isomers (IIIB). The ions $[Ar_2PbOCOCH_3]^+$ and $[ArPb(OCOCH_3)_2]^+$ are dominant in the mass spectra of both compounds. $[(C_6H_5)_3Pb]^+$ may be important but not $[(C_7H_7)_3Pb]^+$ (481) and in neither case is $[Pb(OCOCH_3)_3]^+$ (385) observed. (See Tables 7 and 9). In acetic acid solution these partially acetoxylated derivatives are converted to diaryllead diacetate and lead(II) acetate.

TABLE 7

MASS SPECTRUM OF $(C_6H_5)_3Pb_2(OCOCH_3)_3$ (MASS 822)

m/e	Intensity^a	Identification^b	*m/e*	Intensity^a	Identification^b
208	87	$[Pb]^{\cdot+}$	491^f	3	$[PhPb_2]^+$
225^c	15	$[PbOH]^+$	507	58	$[PhPb_2O]^+$
267	100	$[PbOAc]^+$	522	4	$[PhPb_2OCH_3]^{\cdot+}$
285	47	$[PhPb]^+$	532	s	?
301	1	$[PhPbO]^+$	584	1	$[Ph_2Pb_2O]^{\cdot+}$
311	s	?	602	0.5	?
344	3	$[PhPbOAc]^{\cdot+}$	618	s	?
361^d	0.5	$[Ph_2Pb]^{\cdot+}$ (362)	633	12	$[Ph_2PbC_5H_6]^+$?
403	22	$[PhPb(OAc)_2]^+$	704^h	2	$[Ph_2Pb_2(OAc)_2OH]^+$ (703)
421	87	$[Ph_2PbOAc]^+$	717	s	$[Ph_2Pb(OAc)_2OCH_3]^+$
439^e	45	$[Ph_3Pb]^+$	735	s	$[Ph_3Pb_2(OAc)OCH_3]^+$
455^f	0.5	$[Ph_3PbO]^+$	745	0.5	$[Ph_2Pb_2(OAc)_3]^+$
470^g	0.5	$[Pb_2C_2O_2]^+$	763	3	$[Ph_3Pb_2(OAc)_2]^+$

[a] Intensities of the main isotopic peak relative to the largest peak. Significant but small (< 0.5) peaks are indicated s. [b] Tentative identification based upon lead content. [c] This could be 224 $[PbO]^{\cdot+}$. [d] This could be 361 $[PhPb(OAc)OH]^+$. [e] This could be 439 $[Ph_2Pb(OAc)OH_2]^+$. [f] Distorted isotopic due to overlap with other unidentified lead-containing species. [g] This does not appear to be 470 $[Ph_3PbOCH_3]^{\cdot+}$. [h] This could be 704 $[Ph_3Pb_2OAc]^{\cdot+}$.

TABLE 8

MASS SPECTRUM OF $(C_6H_5)_6Pb_2$ (MASS 878)

m/e	Intensity^a	Identification^b	*m/e*	Intensity^a	Identification^b
285	100	$[PhPb]^+$	516	48	$[Ph_4Pb]^+$
362	3	$[Ph_2Pb]^{\cdot+}$	568	1	$[Ph_2Pb_2]^+$
439	97	$[Ph_3Pb]^+$	645	9	$[Ph_3Pb_2]^+$

[a,b] See footnotes of Table 7.

The important role of acetic anhydride on the preservation of the Pb–Pb bond in the formation of these partially acetoxylated derivatives is far from clear. It is evident however, that a more searching development of this procedure could lead to

TABLE 9

MASS SPECTRUM OF $(p\text{-}CH_3C_6H_4)_3Pb_2(OCOCH_3)_3$ (MASS 864)

m/e	Intensity[a]	Identification[b]	*m/e*	Intensity[a]	Identification[b]
208	53	$[Pb]^{\cdot +}$	497	5	$[T_3PbO]^+$
224[c]	10	$[PbO]^{\cdot +}$	529[d]	3	?
239	0.5	$[PbOCH_3]^+$	560[d]	2	?
267	100	$[PbOAc]^+$	590[d]	1	?
299	25	$[TPb]^+$	612	s	$[T_2Pb_2O]^+$
315	1	$[TPbO]^+$	643	s	$[T_2Pb_2O(OCH_3)]^+$
358	4	$[TPbOAc]^{\cdot +}$	655	s	$[T_2Pb_2OAc]^+$
390	s	$[T_2Pb]^{\cdot +}$	745	s	$[T_2Pb_2(OAc)_2OCH_3]^+$
417	58	$[TPb(OAc)_2]^+$	773	s	$[T_2Pb_2(OAc)_3]^+$
449	89	$[T_2PbOAc]^+$	805	s	$[T_3Pb_2(OAc)_2]^+$

[a,b] See footnotes of Table 7; T = p-tolyl. [c] This could be 225 $[PbOH]^+$. [d] Distorted isotopic due to overlap with other unidentified lead-containing species.

the preparation of the related species, $Ar_5Pb_2OCOCH_3$ and $Ar_4Pb_2(OCOCH_3)_2$ and the corresponding tin compounds. With these in hand more definitive statements about the structure of the derivatives obtained and the nature of intermediates in the acetolysis reaction could be made.

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