# CLEAVAGE OF HEXAPHENYLDILEAD BY MERCURIC SALTS

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SUMMARY

The reactions of hexaphenyldilead with mercuric chloride and with mercuric acetate in 15/1 v/v dioxane–methanol at 30° have been examined. Kinetic and product composition data have been shown consistent with an initial electrophilic C–Pb bond cleavage yielding a pentaphenyldilead followed by two competing reactions. One involves further C–Pb bond cleavage followed by decomposition, while the other involves Pb–Pb bond cleavage yielding an unstable (triphenylplumbyl)mercury intermediate.

## INTRODUCTION

Unlike its reactions with some other metal salts, the reaction of hexaethyldilead with mercuric chloride is reported to be relatively simple[1].

$$R_6Pb_2 + HgCl_2 \rightarrow 2R_3PbCl + Hg \tag{1a}$$

$$R_6Pb_2 + 2HgCl_2 \rightarrow 2R_3PbCl + Hg_2Cl_2 \tag{1b}$$
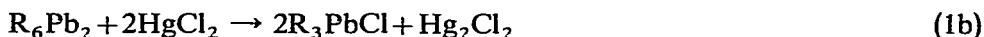
The difference between eqns. (1a) and (1b) clearly arises from the formation of mercurous chloride from the product mercury and the second mercuric chloride reactant.

The most reasonable mechanism for this reaction in our view involves electrophilic Pb–Pb bond cleavage yielding a transient (trialkylplumbyl)mercuric chloride, thus,

$$R_6Pb_2 + HgCl_2 \rightarrow R_3PbCl + [R_3PbHgCl] \rightarrow R_3PbCl + Hg \tag{2}$$

We have previously suggested[2] that several C–Pb bond cleavages occur in the acetolysis of hexaaryldileads while the Pb–Pb bond remains intact, so that the choice between the C–Pb and Pb–Pb bonds for electrophilic attack by mercuric salts in these substrates might be finely balanced. With this in mind we have examined the stoichiometry and kinetics of the reactions of mercuric chloride and acetate with hexaphenyldilead.

EXPERIMENTAL

1. *Materials*

Hexaphenyldilead was obtained from Alfa Inorganics and was purified by repeated crystallisation from AR grade chloroform. Other hexaaryldileads were prepared as previously described[2].

AR grade mercuric chloride was further purified by sublimation, but AR grade mercuric acetate was employed without further purification. Dioxane and methanol were purified following the procedures of Vogel[3].

2. *Kinetic measurements*

Reactions with both mercuric chloride and acetate were carried out in a dioxane/methanol medium (15/1 v/v). The change in concentration of the hexa-phenyldilead was followed by observation at 294 nm, where there is negligible absorption by the solvent system, by other reactants and by the reaction products. A Shimadzu QV-50 or a Cary-14 Spectrometer was employed and the cell compartment was thermostatted at $30.0 \pm 0.1$, $35.0 \pm 0.1$ or $40.0 \pm 0.1°$ as required. For the kinetic studies of the other hexaryldileads the appropriate UV absorption maximum (see ref. 2) was observed. Separate solutions of the required quantities of hexaphenyldilead in dioxane and the mercuric salt in methanol were prepared and, since the solvent mixing process is endothermic, these were thermostatted at $33.5°$ before thorough mixing and transference to the cell of the spectrophotometer.

3. *Product examination*

Material precipitated during the reaction was collected and thoroughly washed with AR grade chloroform followed by dry ethanol to remove organolead and organomercury compounds. Lead(II) chloride dissolved in hot water, precipitated on cooling and was further identified by conversion to the iodide. Mercurous salts were identified by the formation of mercury on treatment with concentrated ammonia solution. The metallic residue was identified as lead by its dissolution in dilute nitric acid and conversion to lead iodide, or as mercury by its lack of reactivity towards dilute nitric acid.

Products soluble in the reaction medium were investigated qualitatively by means of thin-layer chromatography on Silica Gel and using plates coated to a thickness of 0.5 mm. The plates were activated by heating for one hour at ca 150° before use. Benzene/hexane (1/4 v/v) and benzene/methanol (5/1 v/v) gave satisfactory resolution of the various species present. Aqueous potassium permanganate (0.1 $M$) was employed for colour development.

Quantative analysis of the reaction product for triphenyllead, diphenyllead and phenylmercury species was carried out using the diphenylthiocarbazone (di-thizone) complexes, essentially following the method of Henderson and Snyder[4]. This involves the formation of dithizone complexes and their extraction into chloroform solution. The spectrum of this solution in the 400–500 nm range is then compared with that of a blank. The procedure requires the use of blackened vessels in subdued light. All the mercury(II) originally in the system had been consumed in the reaction and therefore did not interfere. Mercury(I), metallic mercury, lead(II) and metallic lead were found to be insufficiently soluble to cause any interference. The four wave-

## TABLE 1

ABSORBANCE OF DITHIZONE COMPLEXES

| Species assayed | $\lambda$ (nm)[a] | | | |
|---|---|---|---|---|
| | 400 | 420 | 450 | 480 |
| $(C_6H_5)_3Pb^+$ | 0.58 | 0.84 | 0.81 | 0.43 |
| $(C_6H_5)_2Pb^{2+}$ | 0.36 | 0.62 | 1.32 | 2.02 |
| $C_6H_5Hg^+$ | 0.21 | 0.48 | 1.00 | 1.30 |

[a] $10^{-3}$ $M$ solutions in chloroform (1 cm cells).

lengths selected for the analysis are given in Table 1 with the absorption data for the three species assayed.

RESULTS

## 1. *Kinetics*

The first series of kinetic measurements were carried out with initial mercuric chloride to hexaphenyldilead ratios of 1/1, 2/1, and 3/1. Only in the latter case did the hexaphenyldilead completely react, and the reciprocal concentration *vs.* time date

## TABLE 2

MERCURIC CHLORIDE CLEAVAGE OF $(C_6H_5)_6Pb_2$

$(C_6H_5)_6Pb_2 + nHgCl_2$; dioxane/methanol (15/1); $30°C \pm 0.1$; $[(C_6H_5)_6Pb_2]_0 = 0.5 \times 10^{-4}$ $M$; $[HgCl_2]_0 = n[Ph_6Pb_2]_0$.

| Time (sec) | Absorbance at 294 nm | | | |
|---|---|---|---|---|
| | $n=1.0$ | $n=2.0$ | $n=2.5$ | $n=3.0$ |
| 0 | 1.57 | 1.57 | 1.57 | 1.57 |
| 120 | 1.40 | 1.32 | | |
| 300 | 1.34 | 1.10 | 1.08 | 0.99 |
| 600 | 1.25 | 0.90 | 0.86 | 0.70 |
| 900 | 1.16 | 0.77 | 0.72 | 0.54 |
| 1200 | 1.10 | 0.70 | 0.61 | 0.43 |
| 1500 | 1.08 | 0.66 | 0.53 | 0.39 |
| 1800 | 1.07 | 0.62 | 0.48 | 0.32 |
| 2400 | 1.05 | 0.56 | 0.43 | |
| $\infty$ | 1.02 | 0.48 | 0.24 | 0.00 |

follow a second order kinetic pattern. In the other cases approximately one third and two thirds of the substrate were consumed. Typical absorbance *vs.* time data are given in Table 2. This indicates a stoichiometry corresponding to eqn. (3) with $n \simeq 3$;

$$Ar_6Pb_2 + nHgCl_2 \rightarrow products \qquad (3)$$

and a rate controlling step first order in hexaphenyldilead and first order in mercuric chloride, leading to the kinetic expression (4);

$$-d[Ar_6Pb_2]/dt = k_{obs} \cdot [Ar_6Pb_2] \cdot (HgCl_2)$$
$$= n \cdot k_{obs} \cdot [Ar_6Pb_2]^2 \tag{4}$$

when

$$[Ar_6Pb_2]_0/[HgCl_2]_0 = 1/n$$

Subsequent detailed stoichiometric studies showed that $n = 2.85$, but it was found possible to obtain satisfactory second order rate constants employing a 3/1 ratio of the reactants. These are summarised in Table 3, which illustrates the effect of temperature change and of added salts.

The data for the reaction where a 2/1 ratio of reactants was employed were examined by the standard integrated expression for a second order process, first order in each reactant.

$$\log\left[\left(\frac{b}{n} - x\right)/(a-x)\right] = (b \cdot n \cdot a) \cdot k \cdot t + \log\left(\frac{b}{n} \cdot a\right)$$

where

$$a = [(C_6H_5)_6Pb_2]_0; \quad b = [HgCl_2]_0; \quad x = [(C_6H_5)_6Pb_2]_t; \quad n = 2.85$$

TABLE 3

MERCURIC CHLORIDE CLEAVAGE OF $(C_6H_5)_6Pb_2$[a]

| Temperature[b] | Concentration (M) | | $k_{obs}$ $(M^{-1} \cdot sec^{-1})$ |
|---|---|---|---|
| | LiClO$_4$ | LiCl | |
| 30.0 | 0 | 0 | $15.4 \pm 0.5$ |
| 30.0 | $10^{-3}$ | 0 | $15.0 \pm 0.5$ |
| 30.0 | 0 | $10^{-3}$ | $12.2 \pm 0.4$ |
| 30.0 | 0 | $10^{-2}$ | $5.5 \pm 0.2$ |
| 35.0 | 0 | 0 | $24 \pm 1$ |
| 40.0 | 0 | 0 | $38 \pm 1$ |

[a] Initial concentrations: $(C_6H_5)_6Pb_2$ $0.5 \times 10^{-4}$ $M$ : $HgCl_2$ $1.5 \times 10^{-4}$ $M$. [b] $\pm 0.1°$

Fig. 1 demonstrates that this expression is followed for more than 80% of the extent of reaction. The rate constant obtained in this way is 15.1 $M^{-1} \cdot sec^{-1}$ (cf. Table 3).

The temperature effect corresponds to an activation energy of 18 kcal/mole. There does not appear to be a significant ionic strength effect but there is a rate decrease due to added chloride that corresponds to the formation of the unreactive $HgCl_3^-$ species with a formation constant of ca. $2 \times 10^2$ $M^{-1}$.

A series of substituted hexaphenyldileads were also examined at 1/3 ratio of reactants. Satisfactory second order rate constants were obtained and these are given in Table 4. Correlation with either the Hammett $\sigma$ of $\sigma^+$ values[5] is satisfactory and gives $\rho = -4.5$. The $p$-methoxy derivative, which would distinguish between a $\sigma^+$ and a $\sigma$ dependence, is extremely reactive and could not be studied even in the presence of added chloride.
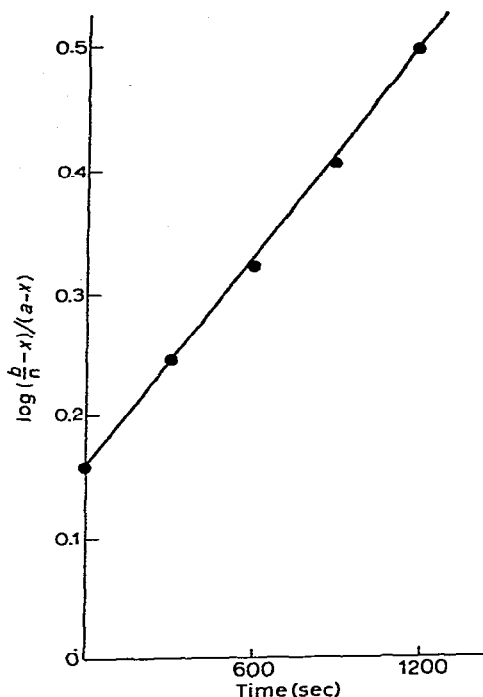
Fig. 1. $(C_6H_5)_6Pb_2 + HgCl_2$ at $\frac{1}{2}$ ratio.

TABLE 4

MERCURIC CHLORIDE CLEAVAGE OF $(XC_6H_4)_6Pb_2$ AT 30.0°

| X | $k_{obs}$ $(M^{-1} \cdot sec^{-1})$ |
|---|---|
| $p$-CH$_3$ | 90 |
| $m$-CH$_3$ | 25 |
| H | 15 |
| $p$-Cl | 0.9 |
| $m$-Cl | 0.5 |

Hexaphenyldilead reacts similarly with mercuric acetate but very much more rapidly. At 30° in the 15/1 dioxane/methanol medium with $(C_6H_5)_6Pb_2$/Hg-$OCOCH_3)_2 = 1/2.5$ after two minutes 94% of the $5 \times 10^{-5}$ $M$ hexaphenyldilead has been consumed. Typical absorbance vs. time data are given in Table 5.

Tetraphenyllead and triphenyllead chloride also react with mercuric chloride under these conditions, but their rate constants, 0.37 and 0.33 $M^{-1} \cdot sec^{-1}$ respectively, are almost fifty times smaller than that of hexaphenyldilead.

### Stoichiometry

The stoichiometries of the hexaphenyldilead reactions with mercuric chloride and with mercuric acetate were examined in detail firstly by determination of the extent of reaction for various ratios of reactants (See Table 6). The fraction of substrate

TABLE 5

MERCURIC ACETATE CLEAVAGE OF $(C_6H_5)_6Pb_2$

$(C_6H_5)_6Pb_2 + nHg(OCOCH_3)_2$; dioxane/methanol (15/1); $30°C \pm 0.1$; $[(C_6H_5)_6Pb_2]_0 = 0.5 \times 10^{-4}$ $M$; $[Hg(OCOCH_3)_2]_0 = n \cdot [(C_6H_5)_6Pb_2]_0$.

| Time (sec) | Absorbance at 294 nm | | |
|---|---|---|---|
| | $n = 1.0$ | $n = 2.0$ | $n = 2.5$ |
| 0 | 1.57 | 1.57 | 1.57 |
| 120 | 0.97 | 0.27 | 0.10 |
| 480 | 0.96 | | |
| 1140 | 0.94 | | |
| 1500 | | 0.26 | 0.00 |
| 2160 | 0.93 | | |
| 3000 | | 0.25 | |
| ∞ | 0.90 | 0.25 | |

TABLE 6

EXTENT OF REACTION FOR VARIOUS REACTANT RATIOS

Dioxane/Methanol (15/1); $30°$.

| $(C_6H_5)_6Pb_2/HgX_2$ | Fraction $(C_6H_5)_6Pb_2$ consumed | |
|---|---|---|
| | $X = Cl$ | $X = OCOCH_3$ |
| 1/1.0 | 0.35 | 0.425 |
| 1/1.5 | 0.52 | 0.63 |
| 1/2.0 | 0.70 | 0.84 |
| 1/2.5 | 0.87 | 1.00 |
| 1/3.0 | 1.00 | 1.00 |

consumed is essentially linearly related to the amount of electrophile and the ratios required for complete consumption are 2.85 and 2.35, respectively, for the mercuric chloride and acetate. Further reaction of excess electrophile takes place with the reaction products.

The product of the mercuric chloride reaction at 1/3 ratio contains triphenyl-lead chloride, diphenyllead dichloride, lead(II) chloride, lead, diphenylmercury, phenylmercury chloride and mercurous chloride but does not contain tetraphenyl-lead nor mercury. On the other hand the mercuric acetate reaction at 1/3 ratio yields triphenyllead acetate, diphenyllead diacetate, lead(II) acetate, phenylmercury acetate and mercury. Again tetraphenyllead is absent but so also is diphenylmercury and lead.

Three of these products can be determined by observation of the spectrum of dithizone complexes. Table 8 shows the observed absorbances at four wavelengths and the values calculated for product composition expected for the mechanism suggested below.

DISCUSSION

The kinetic form, the effect of substituents and what precedents there are, *e.g.* the protolysis of hexaaryldileads[2], suggest that the initial and rate controlling step is the electrophilic cleavage of a C−Pb bond.

$$Ar_6Pb_2 + HgX_2 \rightarrow Ar_5Pb_2X + ArHgX \tag{5}$$
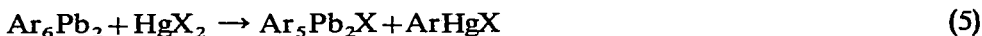
This must be followed by several fast steps leading to the final products and consuming additional mercuric species.

From the fact that a non-integral stoichiometric quantity of the mercuric species is required, there must be at least two pathways with different overall requirements of mercuric species, but since the stoichiometry does not vary with reactant ratio these pathways have the same kinetic dependence on the mercuric species, *e.g.* both first order or both zero order.

The formation of metallic mercury or lead suggests that one of these pathways (Path I) is that given in eqn. (6).

$$Ar_5Pb_2X + HgX_2 \rightarrow [Ar_3PbHgX] + Ar_2PbX_2$$

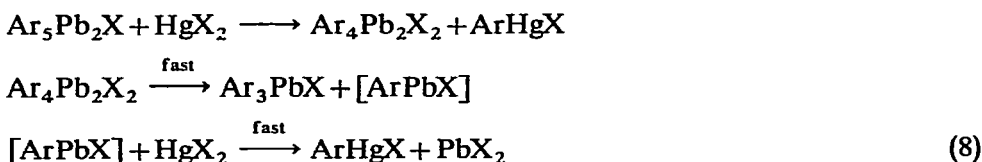$$[Ar_3PbHgX] \xrightarrow{\text{fast}} Ar_3PbX + Hg \tag{6}$$
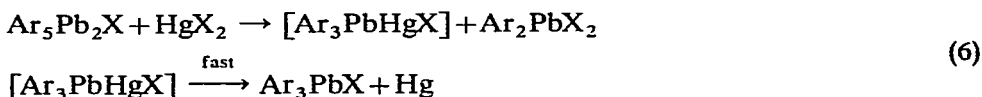
At this point the difference between the products of mercuric chloride and acetate reactions arises since metallic mercury can undergo further reaction with triphenyllead chloride according to eqn. (7) but not with the acetate[6].

$$2\,Ar_3PbCl + 5Hg \rightarrow 3\,Ar_2Hg + Hg_2Cl_2 + 2\,Pb \tag{7}$$
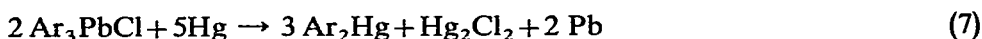
Whereas metallic mercury only is formed in the acetate reaction, the chloride reaction yields metallic lead, mercurous chloride and diphenylmercury at the expense of some of the triphenyllead chloride.

We suggest that the second reaction path (Path II) is the further C−Pb reaction of the initial pentaphenyldilead species, followed by its rapid decomposition possibly via an organic lead(II) species which reacts rapidly with the mercuric species.

$$Ar_5Pb_2X + HgX_2 \longrightarrow Ar_4Pb_2X_2 + ArHgX$$

$$Ar_4Pb_2X_2 \xrightarrow{\text{fast}} Ar_3PbX + [ArPbX]$$

$$[ArPbX] + HgX_2 \xrightarrow{\text{fast}} ArHgX + PbX_2 \tag{8}$$

Similar steps were suggested for the acetolysis reaction[2].

Regarding the formation of $Ar_3PbHgX$ we cannot distinguish kinetically between the two step sequence, (5) and (6), given above and a single step initial Pb−Pb cleavage reaction,

$$Ar_6Pb_2 + HgX_2 \xrightarrow{a'} Ar_3PbHgX + Ar_3PbX \tag{9}$$
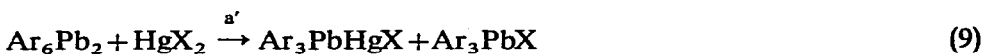
which would give:

$$k_{obs} = k_a + k'_a \tag{10}$$

However reaction (5) provides a source of $Ar_2PbX_2$ which must otherwise arise from the reaction of $Ar_3PbX$ with further mercuric species.

     Fig. 2 summarises the suggested reaction pathways and includes reaction (9). Setting the ratio $k_a/(k_a+k'_a)=\alpha$ and the ratio Path I/Path II $=k_b/k_c=\beta/(1-\beta)$, the composition of the reaction products from an initial quantity $0.5 \times 10^{-3}$ moles of
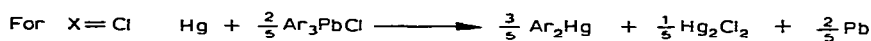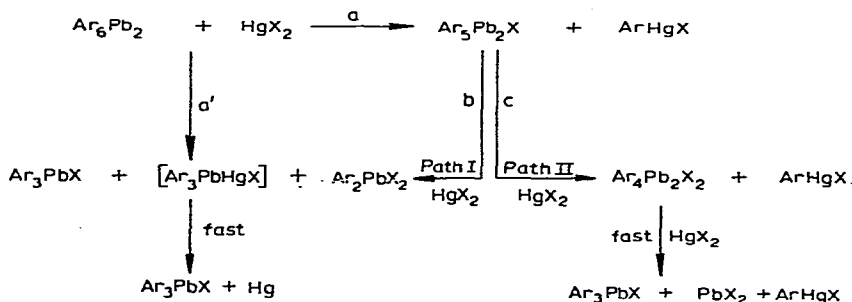


For $X = Cl$     $Hg + \frac{2}{5}Ar_3PbCl \longrightarrow \frac{3}{5}Ar_2Hg + \frac{1}{5}Hg_2Cl_2 + \frac{2}{5}Pb$

Fig. 2.

TABLE 7

CALCULATED PRODUCT COMPOSITION

| Product | Yield ($10^{-3}$ M) | X=Cl[b] | | X=OCOCH₃[b] | |
|---|---|---|---|---|---|
| | | a | b | a | c |
| $Ar_3PbX$ | $1-0.5\,\alpha$ | $1-0.5\,\alpha$ | $1.095-0.7\,\alpha$ | $1-0.5\,\alpha$ | $0.675-0.5\,\alpha$ |
| $Ar_2PbX_2$ | $0.5\,\alpha\cdot\beta$ | $\alpha-0.925$ | $\alpha-0.85$ | $\alpha-0.675$ | $\alpha-0.35$ |
| $PbX_2$ | $0.5\,\alpha-0.5\,\alpha\cdot\beta$ | $0.925-0.5\,\alpha$ | $0.925-0.5\,\alpha$ | $0.675-0.5\,\alpha$ | $0.675-0.5\,\alpha$ |
| Pb | 0 | 0 | $0.2\,\alpha-0.17$ | 0 | 0 |
| $Ar_2Hg$ | 0 | 0 | $0.3\,\alpha-0.255$ | 0 | 0 |
| ArHgX | $1.5\,\alpha-\alpha\cdot\beta$ | $1.85-0.5\,\alpha$ | $1.925-0.5\,\alpha$ | $1.35-0.5\,\alpha$ | $1.675-0.5\,\alpha$ |
| $Hg_2X_2$ | 0 | 0 | $0.1\,\alpha-0.085$ | 0 | 0 |
| Hg | $0.5-0.5\,\alpha+0.5\,\alpha\cdot\beta$ | $0.5\,\alpha-0.425$ | 0 | $0.5\,\alpha-0.175$ | $0.5\,\alpha-0.175$ |
| $HgX_2$ consumed | $0.5+\alpha-0.5\,\alpha\cdot\beta$ | 1.425 | 1.5 | 1.175 | 1.5 |

[a] Initial $[Ar_6Pb_2]=0.5 \times 10^{-3}$ M. [b] a, Without allowance for reaction (7) and excess $HgX_2$; b, With allowance for reaction (7) and excess $HgX_2$; c, With allowance for excess $HgX_2$.

hexaphenyldilead may be deduced (See Table 7). From the stoichiometric requirements of mercuric chloride and acetate the unknown $\beta$ may be eliminated since,

    for $X = Cl$        $1.425 = 0.5+\alpha-0.5\alpha\cdot\beta$

                   $\therefore\;\; \alpha\cdot\beta = 2\alpha-1.85$

    for $X = OCOCH_3$    $1.175 = 0.5+\alpha-0.5\alpha\cdot\beta$.

                   $\therefore\;\; \alpha\cdot\beta = 2\alpha-1.35$

and the product composition can be expressed in terms of $\alpha$ as the only unknown. After allowance for reaction (7) and the consumption of excess mercuric species, the absorption spectrum of the product may be compared with that calculated to yield values for the unknown $\alpha$. (The data for 480 nm were used). For the mercuric chloride reaction it is found that $\alpha = 0.98$, and for the mercuric acetate reaction $\alpha = 0.99$. This shows that within the experimental uncertainty reaction (9) makes no significant contribution, certainly less than 5% of the total reaction, and may be neglected.

As a test of the suggested mechanism the observed absorption spectrum and that calculated for the appropriate $\beta$ values with allowance for reaction (7) and for the reaction of excess electrophile, are compared in Table 8. The agreement is seen to be satisfactory and it is difficult to imagine an alternative *simple* mechanism that can account for the observed product composition.

The corresponding reactions of hexaalkyldileads appear to take place considerably more rapidly and exclusively with initial Pb—Pb bond cleavage. The pre-

TABLE 8

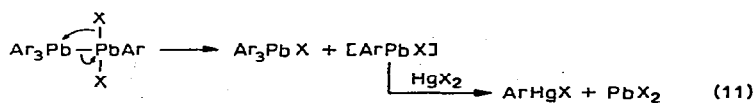ABSORBANCE OF MIXTURE OF DITHIZONE COMPLEXES OF PRODUCTS

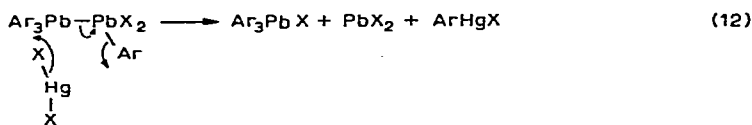| Complex | | $\lambda$ (nm)[a] | | | |
|---|---|---|---|---|---|
| | | 400 | 420 | 450 | 480 |
| $HgCl_2$ (3/1) | Obsd. | 0.59 | 1.10 | 1.95 | 2.30 |
| Reaction product | Calcd. | 0.58 | 1.11 | 1.93 | 2.30 |
| $Hg(OCOCH_3)$ (3/1) | Obsd. | 0.58 | 1.00 | 2.10 | 2.90 |
| Reaction product | Calcd. | 0.58 | 1.10 | 2.00 | 2.90 |

[a] $10^{-3}$ $M$ solutions in chloroform (1 cm cell).

ferred C—Pb cleavage in the present case therefore seems to be more associated with reduced Pb—Pb bond reactivity, perhaps for steric reasons, than enhanced C—Pb reactivity.

Decomposition of the primary product by Path I accounts for 15% of the reaction ($\beta = 0.15 \therefore k_c \simeq 6k_b$) in the case of mercuric chloride, but 65% in the acetate case ($\beta = 0.65 \therefore k_b \simeq 2k_c$). There can be several reasons for this, but it is instructive that tetraphenyllead and triphenyllead chloride have similar reactivities towards mercuric chloride. Perhaps the C—Pb cleavage rate ($k_c$) of the pentaphenyldilead chloride is not reduced relative to that for hexaphenyldilead wheras in the corresponding acetate C—Pb reactivity is reduced below Pb—Pb reactivity.

The tetraphenyldilead species formed in Path II can be formulated in two ways. In view of the fact that a triphenyllead derivative must be obtained from it, the most reasonable formulation and subsequent reaction is that given in eqn. (11) or (12).

$$Ar_3Pb-PbAr \longrightarrow Ar_3Pb\,X + [ArPbX]$$
$$\qquad\qquad \downarrow HgX_2$$
$$\qquad\qquad ArHgX + PbX_2 \qquad (11)$$

$$Ar_3Pb - PbX_2 \longrightarrow Ar_3Pb\,X + PbX_2 + ArHgX \qquad (12)$$

with the bridging structure:
$$\begin{array}{c} X\\ | \\ Hg \\ | \\ X \end{array}$$

However we have previously suggested[2] that the isomeric structure is more likely for the electrophilic C–Pb cleavage and we are forced to tentatively suggest the following alternative.

$$Ar - Pb - Pb - X \longrightarrow ArHgX + PbX_2 + Ar_3Pb\,X \qquad (13)$$
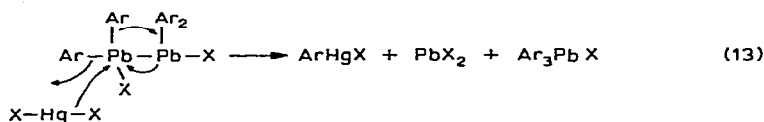
The C–Pb cleavage may however be concerted with the Pb–Pb cleavage in Path II as follows:

$$Ar_3Pb - Pb - Ar \longrightarrow Ar_3PbX + ArHgX + [ArPbX]$$
$$[ArPbX] \xrightarrow{HgX_2} ArHgX + PbX_2$$
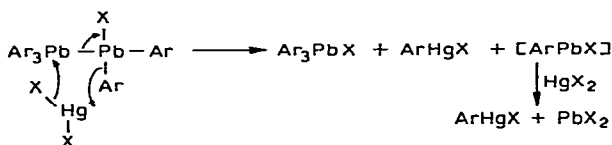
without the intermediacy of $Ar_4Pb_2X_2$.

ACKNOWLEDGEMENTS

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