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HEXAMETHYLDILEAD

II *. REACTIONS WITH TRIMETHYLLEAD AND TRIMETHYLTIN CHLORIDES

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Summary

Hexamethyldilead reacts with trimethyltin chloride or trimethyllead chloride to yield tetramethyltin and/or tetramethyllead and lead(II) chloride three to four powers of ten more rapidly than hexamethylditin. The rate controlling step is Pb—CH_3 cleavage and it is suggested that dimethyllead is formed either subsequently or simultaneously as a transient intermediate. Rate constants are also reported for the reactions of tetramethyllead and trimethyl-t-butyllead.

Introduction

The first product of many reactions of hexaalkyldileads is likely to be a trialkyllead salt, which can then undergo further reaction. Such species are also frequent byproducts or unchanged starting materials and can be responsible for reduced yields in the syntheses of hexaalkyldileads. The importance of these reactions to thermolysis in carbon tetrachloride solution and to methanolysis was indicated in Part I [1].

The reaction between hexaethyldilead and triethyllead bromide according to,

$$(C_2H_5)_6Pb_2 + 2\ (C_2H_5)_3PbBr \rightarrow 3\ (C_2H_5)_4Pb + PbBr_2$$

was reported by Razuvaev, Dergunov and Vyazankin [2], the reaction being complete in 5 minutes at room temperature in the absence of solvent. These workers also report [3] that hexaethyldilead reacts with triethyltin chloride during twenty-four hours in the dark at room temperature with the following stoichiometry (number of moles reacted or formed).

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$$\begin{array}{lllll} (C_2H_5)_6Pb_2 & + (C_2H_5)_3SnCl & \rightarrow (C_2H_5)_3SnCl & + (C_2H_5)_4Sn & + (C_2H_5)_3PbCl + \\ 0.0091 & 0.0208 & 0.0055 & 0.0073 & 0.0006 \end{array}$$

$$\begin{array}{ll} (C_2H_5)_4Pb & + PbCl_2 \\ 0.0036 & 0.0073 \end{array}$$

Experimental

Materials

Samples of pure hexamethyldilead were obtained as described in Part I [1]. Tetramethyllead was supplied and used as an 80% solution with toluene (Alfa Inorganics). Trimethyllead chloride (Organisch Chem. Inst. T.N.O., Utrecht) was recrystallised from chloroform/hexane. Trimethyllead nitrate was prepared by the action of silver nitrate on tetramethyllead in 2% aqueous methanol. After filtration using a fine paper to remove the precipitated silver, the solvent was evaporated and the crude product recrystallised from chloroform/hexane. Trimethyltin chloride (Alfa Inorganics) was purified by vacuum distillation, b.p. 74—75°C/45 mm Hg.

Trimethyl-t-butyllead was prepared in low yield by addition of 14.4 g (0.05 mol) of trimethyllead chloride in anhydrous tetrahydrofuran, to a two-fold excess of t-butylmagnesium chloride (Alfa Inorganics) in tetrahydrofuran. The chloride was added slowly to avoid any excess which can cause redistributions. The mixture became slightly warm. After all the chloride had been added, the solution was refluxed for an hour, then hydrolysed by adding saturated ammonium chloride solution. Extraction of the organic layer with ether and removal of solvent left an orange liquid containing suspended solid. The product was distilled and the fraction boiling at 47°C/13 mm Hg (lit. [4] 47°C/13 mm Hg) was collected. This material was substantially pure, the NMR spectrum showing the presence of a small amount (ca. 1%) of tetramethyllead. The compound solidified in a refrigerator (m.p. lit. [4] 5.7°C).

Perdeutero-tetramethyllead was prepared by addition under nitrogen, with vigorous stirring, of anhydrous lead chloride (18.5 g, 0.067 mol) to the refluxing Grignard reagent from methyl-d_3 iodide (20 g, 0.14 mol) and magnesium (3.5 g, 0.15 mol) in diethyl ether. The reaction was exothermic, and lead metal precipitated immediately. After refluxing for an hour, water was added and the organic layer extracted with ether. The ether was distilled slowly at atmospheric pressure to leave a clear liquid contaminated with some yellow solid. The crude product was distilled up a glass tube at atmospheric pressure and 100—120°C. (Lit. [5] 110°C/760 mm Hg, Yield 4.66 g (53%).) The PMR spectrum showed no spurious peaks.

Methanol was AJAX UNIVAR "dried for non-aqueous titrations", methyl-d_3 iodide was from Koch—Light, anhydrous tetrahydrofuran was from E. Merck and anhydrous A.R. ether was from Mallinckrodt.

Product examination

Reaction stoichiometries, and some kinetic data, were studied in NMR tubes sealed with serum caps. Peak heights, corrected for the magnetically active isotopes present [1], were compared where possible with an internal reference, e.g.

a known amount of added cyclohexane or a ^{13}C satellite of the solvent, methanol. Alternatively where no loss of metal-bound methyl groups was evident the individual peak heights were compared with their sum. Methyl group balance spectra were recording using JEOL PS-100 or MH-100 spectrometers.

Kinetic measurements

When the PMR spectra were employed to follow reactions these were conducted in NMR tubes sealed with pressure caps and set up as previously described. In most studies the JEOL MH-100 was employed with a probe temperature of 30 (±0.5)°C.

For reactions followed by observation of the UV absorbance of hexamethyldilead ($\epsilon \sim 25\,400$ at 274 nm) solutions of the reactants were brought to the appropriate temperature in a thermostat bath and then the required quantities thoroughly mixed before loading into the cell of a Cary 17 recording spectrometer.

The kinetic treatment of the system perdeutero-tetramethyllead/trimethyllead chloride was achieved as follows. Consideration of all possible reactions, with appropriate statistical factors in the rate constants (the rate constant k is designated as the specific rate for the removal of one methyl group from "tetramethyllead", and including only those "tetramethyllead" ("*TML*") species visible by NMR, leads to the following set of differential equations.

$$\frac{dB}{dt} = 4\,kAR + 2\,kCR + kDR + 2\,kCS + 3\,kDS + 4\,kES - (4\,kP + 4\,kQ + kR + 3\,kS)B \tag{1}$$

$$\frac{dC}{dt} = 4\,kAQ + 3\,kBQ + kDQ + kBR + 3\,kDR + 4\,kER - (4\,kP + 2\,kQ + 2\,kR + 4\,kS)C \tag{2}$$

$$\frac{dD}{dt} = 4\,kAP + 3\,kBP + 2\,kCP + kBQ + 2\,kCQ + 4\,kEQ - (3\,kP + kQ + 4\,kR + 4\,kS)D \tag{3}$$

$$\frac{dE}{dt} = kBP + 2\,kCP + 3\,kDP - (4\,kQ + 4\,kR + 4\,kS)E \tag{4}$$

Where: $A = [(CD_3)_4Pb]$, $B = [(CD_3)_3PbCH_3]$, $C = [(CD_3)_2Pb(CH_3)_2]$, $D = [(CD_3)Pb(CH_3)_3]$, $E = [Pb(CH_3)_4]$, $P = [(CH_3)_3PbCl]$, $Q = [(CH_3)_2Pb(CD_3)Cl]$, $R = [(CH_3)Pb(CD_3)_2Cl]$, $S = [Pb(CD_3)_3Cl]$. Now, since "*TML*" = $(4\,E + 3\,D + 3\,C + B)/4$, then, substituting

$$X = 4\,A + 3\,B + 2\,C + D$$

and $Y = B + 2\,C + 3\,D + 4\,E$,

$$\frac{d(\text{"}TML\text{"})}{dt} = kX(3\,P + 2\,Q + R)/4 - kY(Q + 2\,R + 3\,S)/4 \tag{5}$$

when the equations 1—4 are summed, and terms collected. A material balance on CH_3 groups gives

$$3P_0 = (3P + 2Q + R) + (B + 2C + 3D + 4E)$$

$$\therefore 3P + 2Q + R = 3P_0 - Y$$

Similarly, for CD_3 groups,

$$4A_0 = (4A + 3B + 2C + D) + (Q + 2R + 3S)$$

$$\therefore Q + 2R + 3S = 4A_0 - X$$

$$\therefore \text{from eq. 5, } \frac{d(\text{“}TML\text{”})}{dt} = \frac{1}{4}\frac{dY}{dt} = (kX(3P + 2Q + R))/4 - (kY(Q + 2R + 3S))/4$$

$$\therefore \frac{dY}{dt} = kX(3P_0 - Y) - kY(4A_0 - X)$$

Now, since $P_0 = P + Q + R + S$

and $A_0 = A + B + C + D + E$,

$$\therefore X = 4A + 3B + 2C + D = 4(A + B + C + D + E) - (B + 2C + 3D + 4E)$$

$$= 4A_0 - Y$$

$$\therefore \frac{dY}{dt} = k(3P_0 - Y)(4A_0 - Y) - kY(4A_0 - 4A_0 + Y)$$

$$= k(3P_0 - Y)(4A_0 - Y) - kY^2$$

$$\therefore \frac{d(\text{“}TML\text{”})}{dt} = 3kP_0A_0 - (3P_0 + 4A_0)k(\text{“}TML\text{”})$$

This is a first order kinetic equation, and may be integrated to yield

$$\ln\left[1 - \frac{(3P_0 + 4A_0)}{3A_0P_0}\right](\text{“}TML\text{”}) = -(3P_0 + 4A_0)kt$$

Experimentally, the quantity (“*TML*”) can be related to the ratio of the peak heights of the tetramethyllead and t-butanol used as internal standard.

$$\text{Thus } (\text{“}TML\text{”}) = \frac{3h'_1}{4h_R}[R]$$

where h'_1 = corrected height of tetramethyllead peak, h_R = height of t-butanol peak and [R] = concentration of t-butanol.

$$\therefore \ln\left[1 - \frac{3P_0 + 4A_0}{4A_0P_0}\right]\frac{h'_1}{h_R}[R] = -(3P_0 + 4A_0)kt$$

The plots of the L.H.S. of this equation vs. time showed excellent correlation.

Results

(a) Tetramethyllead and trimethyllead chloride

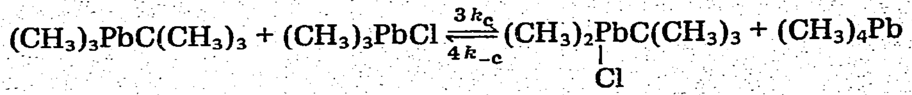
This reaction was made observable by the use of $(CD_3)_4Pb$ and it is assumed that there is no kinetic isotope effect for the cleavage of $Pb{-}CD_3$ vs. $Pb{-}CH_3$. [There is no observable isotope effect on the PMR spectra of $(CH_3)_nPb(CD_3)_{4-n}$]. The reaction is quite fast even at the low concentrations (ca. 0.015 M) employed so that data could only be collected during five minutes of reaction. Good first order behaviour was observed, see Fig. 1, and two kinetic runs at 0.016; 0.016 M and 0.014; 0.017 M initial concentrations gave $4\,k_a = 4.2(\pm 0.2) \times 10^{-1}\ \text{mol}^{-1}\ \text{s}^{-1}$ (30°C).

(b) Tetramethyllead and trimethyltin chloride

As previously reported [6] three kinetic runs for this reaction yielded $4\,k_b = 3.4\ (\pm 0.3) \times 10^{-2}\ \text{mol}^{-1}\ \text{s}^{-1}$ (30°C).

(c) Trimethyl-t-butyllead and trimethyllead chloride

This reaction,



$$(CH_3)_3PbC(CH_3)_3 + (CH_3)_3PbCl \underset{4k_{-c}}{\overset{3k_c}{\rightleftharpoons}} (CH_3)_2\underset{\displaystyle Cl}{\underset{|}{Pb}}C(CH_3)_3 + (CH_3)_4Pb$$

proceeds exclusively with Pb—CH$_3$ cleavage (as judged by the PMR spectrum at high gain) to an equilibrium slightly in favour of the reactants with $K = 3\,k_c/4\,k_{-c} = 0.52(\pm 0.06)$. The reverse reaction becomes kinetically important within ca. three minutes even at low concentrations, ca. 0.01 M. (Kinetic study in the reverse direction would be more informative were it not for the fact that dimethyl-t-butyllead chloride is rather unstable and could not be satisfactorily purified.) The PMR spectrum has some overlaps, but the peaks of the trimethyllead groups of the two reactants are unaffected and are separated by only a few Hz, leaving only a small time lag due to the scan rate between their measurements.

Data from the early part of the reaction give an excellent fit to the usual second order function and the mean of the results of two kinetic runs is $3\,k_c = 2.6(\pm 0.1) \times 10^{-1}\ \text{mol}^{-1}\ \text{s}^{-1}$ and hence $4\,k_{-c} = 5.1(\pm 0.8) \times 10^{-1}\ \text{mol}^{-1}$ (30°C).

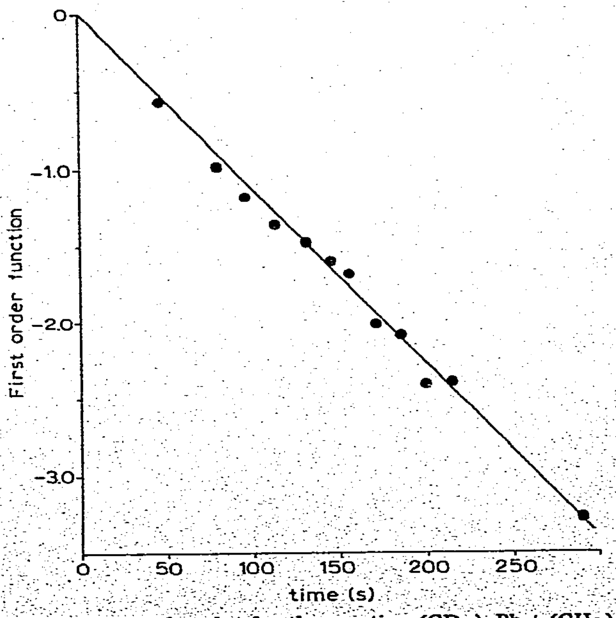


Fig. 1. First order plot for the reaction $(CD_3)_4Pb + (CH_3)_3PbCl$.

(d) Trimethyl-t-butyllead and trimethyltin chloride

The equilibrium in this case lies well to the side of the products and hence the reverse reaction does not interfere. At large extents of reaction the product, dimethyl-t-butyllead chloride, was observed to be undergoing decomposition. (It is sensitive to light as is the corresponding tin compound.) The equilibrium constant could not be determined.

As indicated by the PMR spectrum of a typical reaction mixture, Fig. 2, there are, not surprisingly, a number of coincidences and it proved difficult to find an internal reference that did not interfere with other peaks. Arithmetic manipulation of the various peak heights determined the unknowns of the system, established the stoichiometry, and provided the appropriate quantities for second order treatment. Two kinetic runs gave $3\,k_d = 1.0(\pm 0.2) \times 10^{-2}$ mol^{-1} s^{-1} (30°C).

(e) Hexamethyldilead and trimethyllead chloride

At concentrations in methanol suitable to PMR investigation the reaction had reached completion by the time the first observation could be made. The stoi-

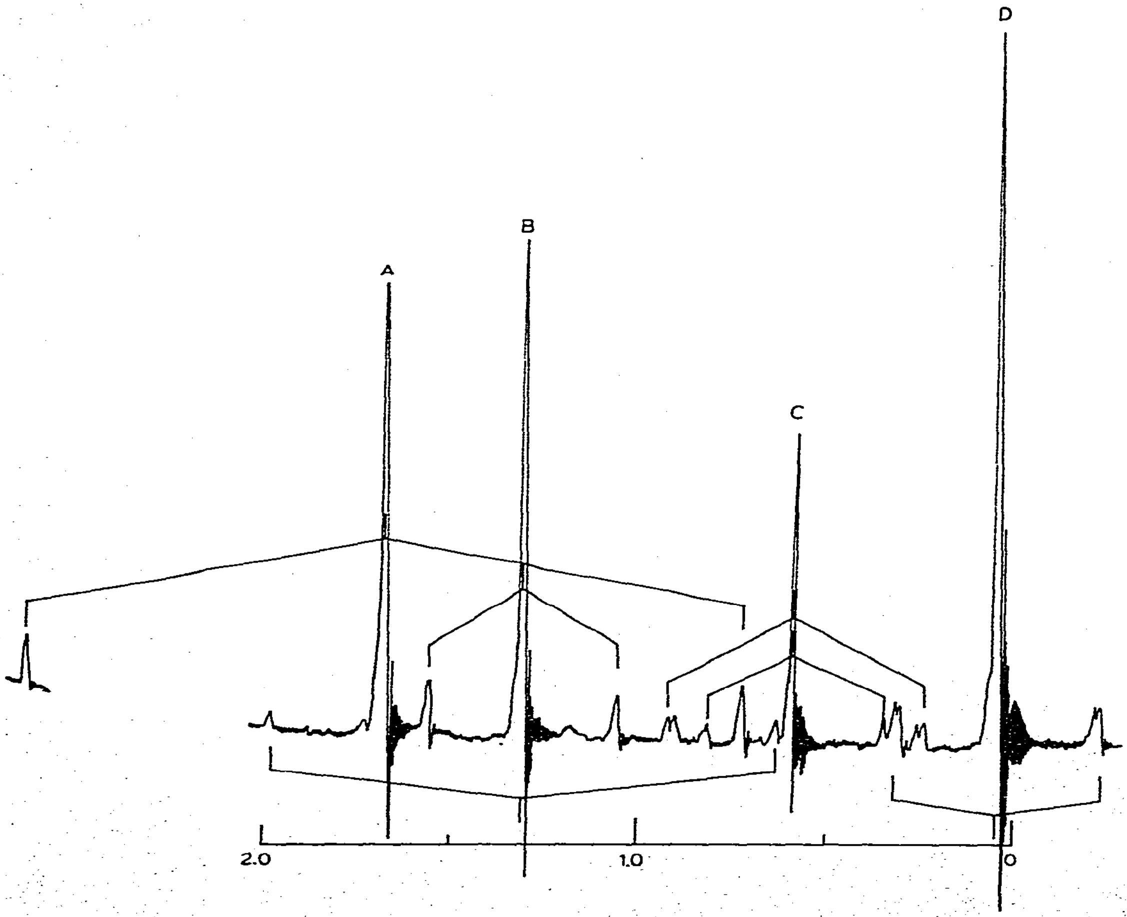


Fig. 2. 100 MHz spectrum of reaction mixture $(CH_3)_3PbC(CH_3)_3$ + $(CH_3)_3SnCl$. A: $(CH_3)_2Pb[C(\underline{CH_3})_3]Cl$; B: $(\underline{CH_3})_2Pb[C(CH_3)_3]Cl$ and $(CH_3)_3PbC(\underline{CH_3})_3$; C: $(\underline{CH_3})_3PbC(CH_3)_3$ and $(CH_3)_3SnCl$; D: $(CH_3)_4Sn$.

chiometry was, however, established as:

$$(CH_3)_6Pb_2 + 2\ (CH_3)_3PbCl \rightarrow 2\ (CH_3)_4Pb + PbCl_2$$

This stoichiometry was similarly shown to apply to the reaction with trimethyllead nitrate and also the hydroxide, methoxide and cyanide, although these latter proceed considerably more slowly and are comparable in rate with methanolysis.

The reaction was therefore followed by means of UV spectroscopy under first order conditions with a sufficiently large excess of trimethyllead chloride, so that precise knowledge of the initial concentration of hexamethyldilead was not required (see above). The results thus obtained showed excellent first order behaviour for at least 90% reaction and are given in Table 1. A plot of the first order rate constants vs. trimethyllead chloride concentration is shown in Fig. 3. (The rate of methanolysis is sufficiently slower to be ignored.) The reaction is not simply first order in the stoichiometric concentration of trimethyllead chloride, $[(CH_3)_3PbCl]_s$, nor is there a half power dependence. On the other hand, the following linear function,

$$k_{obs}/[(CH_3)_3PbCl]_s^{1/2} = a[(CH_3)_3PbCl]_s^{1/2} + b$$

does account for the data as indicated in Fig. 4. (cf. hexamethylditin and trimethyltin chloride [7]) with:

$$[(CH_3)_6Pb_2]_0 = 4.4 \times 10^{-6}\ a = 14.3(\pm 0.7)\ mol^{-1}\,s^{-1};\ b = 0.216(\pm 0.011)\ mol^{-\frac{1}{2}}\,s^{-1}$$

$$[(CH_3)_6Pb_2]_0 = 3.8 \times 10^{-6}\ a = 13.0(\pm 0.9)\ mol^{-1}\,s^{-1};\ b = 0.207(\pm 0.015)\ mol^{-\frac{1}{2}}\,s^{-1}$$

This behaviour corresponds to a dual reagent situation

$$k_{obs} = 6\ k_e\ [(CH_3)_3PbCl] + 6\ k_e'\ [(CH_3)_3Pb^+]$$

with a low concentration of the cationic reagent [$(CH_3)_3Pb^+$ or some solvated form thereof] arising from the dissociation,

$$(CH_3)_3PbCl \rightleftharpoons (CH_3)_3Pb^+ + Cl^-\quad (K_D)$$

$$[(CH_3)_3Pb^+] \simeq K_D^{\frac{1}{2}}\ [(CH_3)_3PbCl]^{\frac{1}{2}}$$

TABLE 1

FIRST ORDER RATE CONSTANTS FOR THE REACTION

$(CH_3)_6Pb_2 + (CH_3)_3PbCl$ (22°C)

$[(CH_3)_6Pb_2]_0$ (*M*)	$[(CH_3)_3PbCl]_0 \times 10^4$ (*M*)	$k_{obs} \times 10^3$ (s^{-1})
4.4×10^{-6}	6	14.5, 13.3[a]
	4	10.3, 10.4
	2	5.96, 5.87
	1	3.45, 3.63
	0.25	1.46, 1.55
3.8×10^{-6}	4.5	10.3
	3.4	8.1
	2.3	6.1
	1.1	3.6

[a] In this set, two runs were performed at each concentration.

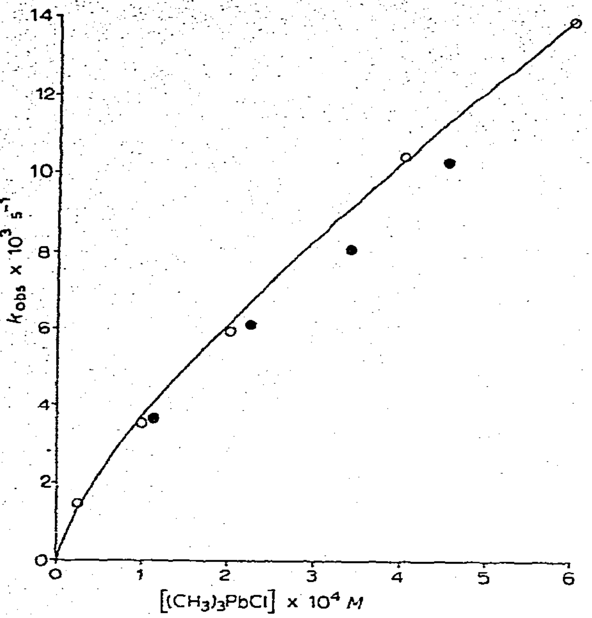


Fig. 3. Plot of k_{obs} vs. $[(CH_3)_3PbCl]$ for the reaction $(CH_3)_6Pb + (CH_3)_3PbCl$.

Thus $a = 6\,k_e = 13.7\ (\pm 1.6)\ \text{mol}^{-1}\ \text{s}^{-1}$ (25°C)

and $b = 6\,(k_e' - k_e)K_D^{\frac{1}{2}} = 0.21\ (\pm 0.03)\ \text{mol}^{-\frac{1}{2}}\ \text{s}^{-1}$ (25°C)

The reaction of hexamethyldilead with trimethyllead nitrate was studied using a Gibson—Durrum stopped-flow apparatus (by kind permission of the Department of Biochemistry). First order conditions were ensured by the use of a large

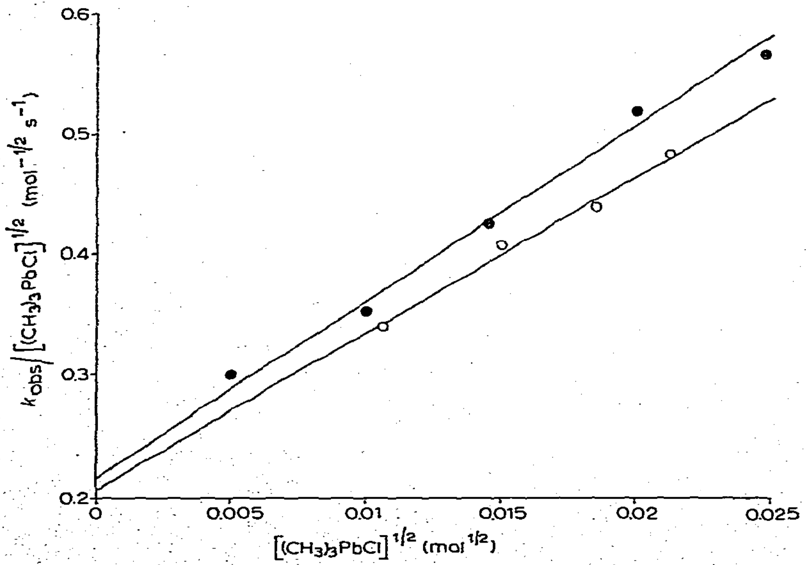


Fig. 4. Plot of $k_{obs}/[(CH_3)_3PbCl]^{\frac{1}{2}}$ vs. $[(CH_3)_3PbCl]^{\frac{1}{2}}$.

concentration of the nitrate. (The chloride could not be studied in this way since, in order to achieve a rate fast enough to avoid diffusion effects in the flow system, a concentration of ca. 10^{-2} *M* was required which gives too great an absorbance due to trimethyllead chloride compared with that of hexamethyldilead.) The first order rate constants obtained from the oscilloscope traces were again found to fit the dual reagent equation above yielding

$$a = 24.05\ (\pm 0.04)\ \text{mol}^{-1}\ \text{s}^{-1};\ b = 1.93\ (\pm 0.01)\ \text{mol}^{-\frac{1}{2}}\ \text{s}^{-1}\ (25^\circ\text{C})$$

(f) Hexamethyldilead and trimethyltin chloride

Again the reaction is complete within the mixing and observation time at PMR concentrations but this technique was employed for stoichiometric studies. A small yield of trimethyllead chloride is observed which may have resulted from the reaction:

$$(CH_3)_4Pb + (CH_3)_3SnCl \rightarrow (CH_3)_3PbCl + (CH_3)_4Sn$$

Assuming this to be the case and correcting the observed concentrations for this reaction and a small amount of tetramethyllead initially present, leads to the following stoichiometry for a typical example.

$$\begin{array}{ccccccccc}
(CH_3)_6Pb_2 & + & (CH_3)_3SnCl & \rightarrow & (CH_3)_4Pb & + & (CH_3)_4Sn & + & PbCl_2 \\
0.0314\,M & & 0.0524\,M & & 0 & & 0 & & 0 \\
\downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\
0 & & 0 & & 0.0324\,M & & 0.0539\,M & & 0.0262\,M
\end{array}$$

The discrepancies here are much larger than we have observed in other cases, but nevertheless we feel the overall reaction to be satisfactory accounted for by

$$(CH_3)_6Pb_2 + 2\ (CH_3)_3SnCl \rightarrow (CH_3)_4Pb + 2\ (CH_3)_4Sn + PbCl_2$$

First order rate constants were obtained as described for the trimethyllead chloride reaction and are summarised in Table 2. While plots of k_{obs} vs. $[(CH_3)_3SnCl]$ and vs. $[(CH_3)_3SnCl]^{\frac{1}{2}}$ show the same type of curvature as in the case of trimethyllead chloride, the dual reagent approach is unsuccessful as anticipated since the value [8] of K_D is too large in this case.

Seven values of K_D in the range 5×10^{-6} to 2×10^{-4} *M* were employed to cal-

TABLE 2

FIRST ORDER RATE CONSTANTS FOR THE REACTION $(CH_3)_6Pb_2 + (CH_3)_3SnCl$ (22°C)

$[(CH_3)_3SnCl]_0 \times 10^3$ *M*	$k_{obs} \times 10^3$ (s^{-1})
13.1	5.8
10.1	4.65
6.55	3.6
3.95	2.7
1.31	1.5
1.23	1.6
0.51	0.825
0.205	0.37
0.1025	0.16

culate the extent of dissociation and the data were examined in terms of

$$k_{obs}/[(CH_3)_3SnCl]_s = 6\ k_f + 6\ (k_f' - k_f)[(CH_3)_3Sn^+]/[(CH_3)_3SnCl]_s$$

Approximately the same linear fit was obtained in each case so that the secon term on the right hand side above could not be determined. However, all sever cases extrapolated to the same value of

$$6\ k_f \simeq 0.1\ mol^{-1}\ s^{-1}.$$

Maximum deviations were observed for the lowest values of $[(CH_3)_3SnCl]_s$ when the extent of dissociation should be the greatest. These were consistent with an association equilibrium

$$(CH_3)_3SnCl + Cl^- \rightleftharpoons (CH_3)_3SnCl_2^-\ (K_A)$$

A small set of kinetic runs were carried out in the presence of added lithium chloride and sufficient lithium perchlorate to give a salt concentration of 0.5 *M* The rate constants are now small enough for methanolysis to be quite significa particularly since it is catalysed by chloride. Correcting the value of k_{obs} for methanolysis, and assuming that dissociation is completely suppressed, yields $6\ k_f \simeq 0.15\ mol^{-1}\ s^{-1}$ in reasonable agreement with the value reported above.

Discussion

A comparison of the rates of Pb—CH₃ cleavage is given in Table 3 and the reactivities of these substrates relative to tetramethyllead are compared with the corresponding tin compounds in Table 4. It can be seen that the steric effect which the t-butyl group presumably exerts on the reactivity of the tin substrate is much smaller in the case of the lead substrates and even negligible for the trimethyllead chloride reaction. In marked contrast again to the corresponding tin substrate, the trimethylplumbyl group has a pronounced activating effect on Pb—CH₃ cleavage. This is a quantitative expression of the general view that hexa alkyldileads are very reactive compounds whereas hexaalkylditins are much like tetraalkyltins as far as their metal—carbon bonds are concerned.

For hexamethyldilead an open transition state with a relatively large separati between lead substrate and reagent is indicated, for then there would be essentially no steric problems for trimethyllead chloride, and very little for trimethylti chloride. Trimethyllead nitrate (undissociated) ($24\ mol^{-1}\ s^{-1}$) is somewhat more

TABLE 3

STATISTICALLY CORRECTED RATE CONSTANTS FOR CLEAVAGE OF Pb—CH₃ BONDS

Substrate	Temperature (°C)	Reagent	
		$(CH_3)_3PbCl$	$(CH_3)_3SnCl$
$(CH_3)_6Pb_2$	22	$k_e = 13.7\ (1.6)\ mol^{-1}\ s^{-1}$	$k_f \sim 0.1$
$(CH_3)_4Pb$	30	$k_a = 0.105\ (\pm 0.005)\ mol^{-1}\ s^{-1}$	$k_b = 8.5\ (\pm 0.8) \times 10^{-3}\ mol^{-1}\ s^{-1}$
		$k_{-c} = 0.13\ (\pm 0.02)\ mol^{-1}\ s^{-1\ a}$	$k = 4.5\ (\pm 0.3) \times 10^{-3}\ mol^{-1}\ s^{-1}$
$(CH_3)_3PbC(CH_3)_3$	30	$k_c = 0.087\ (\pm 0.003)\ mol^{-1}\ s^{-1}$	$k_d = 3.3\ (\pm 0.7) \times 10^{-3}\ mol^{-1}\ s^{-}$

[a] Reaction with $(CH_3)_2Pb[C(CH_3)_3]Cl$. [b] Reaction with $(CH_3)_2Sn[C(CH_3)_3]Cl$ [9]

TABLE 4

REACTIVITIES RELATIVE TO TETRAMETHYLLEAD AND TETRAMETHYLTIN

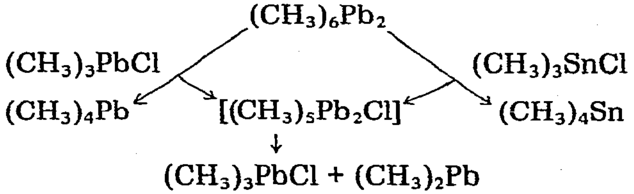
Substrate	Temperature (°C)	Reagent	
		$(CH_3)_3PbCl$	$(CH_3)_3SnCl$
$(CH_3)_6Pb_2$	22	130	~12
$(CH_3)_4Pb$	30	1	1
$(CH_3)_3PbC(CH_3)_3$	30	0.8	0.4
$(CH_3)_6Sn_2$	30[a]	1.5	0.93
$(CH_3)_4Sn$	30[a]	1	1
$(CH_3)_3SnC(CH_3)_3$	30[a]	0.09	0.06

[a] Refs. 6, 7, 9.

reactive towards hexamethyldilead than trimethyllead chloride (14 mol^{-1} s^{-1}) and the trimethyllead cation would seem to be considerably more reactive than both. The value of k_e' arising from the dual reagent treatment cannot be specified in the absence of a value for K_D. The treatment would be obviously unsatisfactory, as in the case of trimethyltin chloride, if K_D were greater than ca. 10^{-6} M for trimethyllead chloride and ca. 10^{-4} for trimethyllead nitrate. Thus k_e' is not less than 2×10^2 mol^{-1} s^{-1}. The activating effect of the trimethylplumbyl group could come into play if substantial positive charge developed on the reacting lead atom. Donor properties for this group are indicated by its effect on ^{13}C chemical shifts [10].

Alternatively the greater reactivity of hexamethyldilead could arise from Pb—Pb bond cleavage occurring in concert with the Pb—CH_3 cleavage. The difference between hexamethylditin and hexamethyldilead would then be associated with the stepwise formation of dimethyltin via pentamethylditin chloride and the one step formation of dimethyllead.

This brings us to a consideration of the reactions subsequent to the initial metal—alkyl group cleavage. In the case of hexamethylditin it is suggested [6] that pentamethylditin chloride dissociates to form dimethyltin which then inserts into Sn—Cl bonds yielding the precursors of the final products $(CH_3)_{2n+2}$-Sn_n, or inserts into trimethyllead chloride yielding dimethyllead after rearrangement and dissociation. The reactions of hexamethyldilead may be similarly described:



$$(CH_3)_2Pb + 2\ (CH_3)_3PbCl \rightarrow 2\ (CH_3)_4Pb + PbCl_2$$

$$\text{or } (CH_3)_2Pb + 2\ (CH_3)_3SnCl \rightarrow 2\ (CH_3)_4Sn + PbCl_2$$

with the further possibility that pentamethyldilead chloride is not an intermediate but rather that dimethyllead is formed in the first step. We envisage that dimethyllead is very rapidly consumed by Pb—CH_3 cleavage reactions with electrophiles. Polymeric "dimethyllead" will not therefore be formed if the intermediate is destroyed in this way faster than it undergoes insertion, and by implication insertion is unfavourable due to the instability of pentamethyldilead chloride. (The converse must necessarily be the case for the corresponding tin compounds.)

In our earlier studies on hexaaryldileads [12] we were at pains to demonstrate that diaryllead and tetraaryllead were not formed in an equilibrium that preceded reaction. (We now believe such a dissociation takes place for hexamethyldilead [1,11] but at a rate much slower than all its reactions with electrophiles including methanol.) Acetolysis showed a substituent effect response typical of protolysis of an aromatic C—Pb bond, but since the hexaaryldileads were found to be very much more reactive than the tetraarylleads a concerted reaction yielding diaryllead may also be involved. However, it must be pointed out that we were able to isolate triaryldilead triacetates, albeit under somewhat different reaction conditions.

The reaction of hexaethyldilead with hydrogen chloride slowly generated from acyl chlorides in methanol solution [13] is now readily understandable in terms of the following steps.

$$(C_2H_5)_6Pb_2 + HCl \xrightarrow{slow} (C_2H_5)_3PbCl + (C_2H_5)_2Pb + C_2H_6$$

$$(C_2H_5)_2Pb + 2\ HCl \xrightarrow{fast} 2\ PbCl_2 + C_2H_6$$

$$(C_2H_5)_6Pb_2 + 2\ (C_2H_5)_3PbCl \xrightarrow{fast} 3\ (C_2H_5)_4Pb + PbCl_2$$

overall

$$(C_2H_5)_2Pb_2 + 2\ HCl \rightarrow (C_2H_5)_4Pb + PbCl_2 + 2\ C_2H_6$$

without the postulation of a prior dissociation forming diethyllead and tetraethyllead. A similar situation is discussed in the following paper (Part III [14]).

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