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A New Type of Complex Reagent, R_4Pb / $TiCl_4$

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Abstract: Tetraalkylleads (R_4Pb) reacted quite smoothly with aldehydes R'CHO in the presence of $TiCl_4$ to produce the corresponding alcohols (RCHOHR') in high to good yields. The reagent system, $R_4Pb/TiCl_4$, exhibited high chemoselectivity; only aldehydes underwent the alkylation in the presence of ketones. Further, the new reagent exhibited high 1,2- and 1,3- asymmetric induction. The transfer order of alkyl groups in the reaction of aldehydes with mixed tetraalkylleads/$TiCl_4$ was determined; Me>Et>i-Pr>>n-Bu.

Introduction

Organomagnesium, lithium, copper compounds are widely used carbanionic alkylating reagents which are useful for the C-C bond formation of carbonyl compounds. Since the mid-1970s, a new current has appeared in this field. Several air-stable, storable, and non-carbanionic reagents, normally used under nonbasic conditions, have been developed. Such reagents include allylic silanes and stannanes. Unfortunately, however, transferable groups of previous non-carbanionic reagents are limited to particular functional groups such as allyl[1b,c], alkynyl[2], and enols[1a]. The transfer of alkyl moiety from group 14 organometallic compounds was entirely unknown despite its potential synthetic importance.[3] Previously we reported that $R_4Pb/TiCl_4$ complex reagent reacted quite smoothly with aldehydes to give the corresponding alkylated alcohol in high yields.[4] We now report full details on the reaction of this reagent system with aldehydes.

Reaction of $R_4Pb/TiCl_4$ with Aldehydes. The reaction of aldehydes with $R_4Pb/TiCl_4$ reagents was examined (Table 1) (eq 1). The transfer of an ethyl group occurred rapidly in essentially quantitative yields (entries 1-3). The transfer of butyl group was relatively slow in comparison with the ethyl transfer (entries 4-7). As shown in entries 4-12, the transfer of secondary alkyl groups such as cyclohexyl and iso-propyl was slow even at 0°C, resulting in low yields of the alkylated products. When the reaction was incomplete (entries 4-12), the starting aldehyde was recovered, and excess Et_4Pb or nBu_4Pb was also recovered in entries 1-7. However, excess $(C_6H_{11})_4Pb$ and iPr_4Pb were not recovered in entries 8-12. It is widely known that the cleavage of C-Pb bond often takes place in the presence of Lewis acids.[5] Perhaps, tetra-sec-alkylleads would be decomposed by the Lewis acid more readily in comparison with tetra-n-alkylleads.

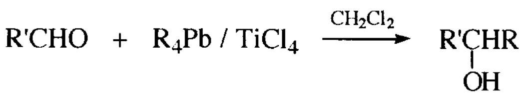
A possibility that RTiLn intervenes as a reactive intermediate seems to be eliminated by the following reasons. The n-alkyl and even sec-alkyl groups underwent the transfer reaction. It is well known that n-alkyl and sec-alkyl titanium reagents of a type $R\text{-}TiCl_3$ easily undergo β-hydride elimination.[6] When $BF_3 \cdot OEt_2$ was used instead of $TiCl_4$, a large excess of Et_4Pb was required to obtain the desired alcohol in good yield. For example, in the reaction of benzaldehyde, the use of 1.4 equiv BF_3 and 2.4 equiv Et_4Pb resulted in 13% yield and the use of 1.1

equiv BF_3 and 16 equiv Et_4Pb gave the ethylated alcohol in 61% yield. Formation of the alcohol by use of BF_3 clearly indicates that transmetallation from R_4Pb to RBLn does not take place at low temperatures (-78°C~-30°C), since RBLn does not alkylate the aldehyde under the reaction conditions.

Table 1. The Reaction of Aldehydes with R_4Pb / $TiCl_4$[a]

			reaction cond		
entry	R_4Pb R	R'CHO R'	temp(°C)	R_4Pb (equiv)	isolated yield of $\underset{\text{OH}}{\text{RCHR}^1}$, %
1	Et	C_6H_5	-78 → -30	1.8	96
2	Et	C_6H_5	-78 → -30	1.3	98
3	Et	$CH_3(CH_2)_6$	-78 → -30	1.3	94
4	nBu	C_6H_{11}	-78 → -30	1.3	70
5	nBu	C_6H_{11}	-78 → 0	1.3	84
6	nBu	$CH_3(CH_2)_6$	-78 → -30	1.3	73
7	nBu	$CH_3(CH_2)_6$	-78 → 0	1.3	88
8	C_6H_{11}	C_6H_{11}	-78 → -30	1.3	32
9	C_6H_{11}	C_6H_{11}	-78 → 0	2.0	38
10	C_6H_{11}	$CH_3(CH_2)_6$	-78 → -30	1.3	41
11	C_6H_{11}	$CH_3(CH_2)_6$	-78 → 0	2.0	46
12	iPr	$CH_3(CH_2)_6$	-78 → 0	2.0	41

[a] $TiCl_4$-CH_2Cl_2 solution (1M, 1.2 equiv) was used.



$$\text{R'CHO} + R_4Pb / TiCl_4 \xrightarrow{CH_2Cl_2} \underset{\text{OH}}{\text{R'CHR}} \qquad \text{(eq 1)}$$

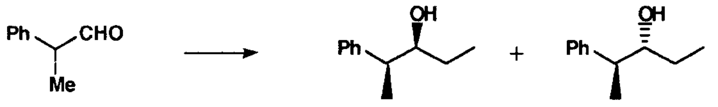
The addition order of R_4Pb, $TiCl_4$, and aldehydes exerts an influence on the yield of the product, also suggesting that RTiLn is not a reactive intermediate. As shown in Table 1, normally, to a CH_2Cl_2 solution of aldehydes was added at -78°C a CH_2Cl_2 solution of $TiCl_4$, and then R_4Pb/CH_2Cl_2 solution was added. On the other hand, a clean reaction did not occur in the case of reversed addition; (i) R_4Pb, (ii) $TiCl_4$ and then (iii) aldehydes. Presumably, transmetallation from R_4Pb to $TiCl_4$ takes place in the reversed addition (eq 2).

$$R_4Pb + TiCl_4 \longrightarrow RTiCl_3 + R_3PbCl \qquad \text{(eq 2)}$$

In fact, it is known that $EtTiCl_3$ can be prepared by treatment of Et_4Pb with $TiCl_4$.[7] Formation of hydride reduction products $R'CH_2OH$ was not observed in the reaction of $R_4Pb/TiCl_4$ with R'CHO, whereas the reaction of n-Bu_4Sn with p-nitrobenzldehyde in the presence of $TiCl_4$ gave p-nitrobenzyl alcohol.[8] Facile transfer of R from R_4Pb in comparison with R_4Sn is due to the weak bondstrength of the C-Pb bond.

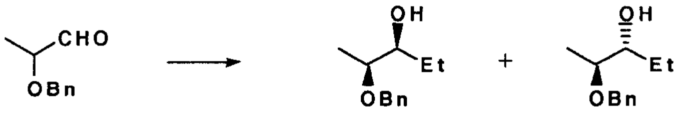
Chemo- and Stereoselective Reactions. The alkylation of aldehydes took place chemoselectively in the presence of ketones. For example, the reaction of n-Bu_4Pb (1.3 mmol)-$TiCl_4$ (2.4 mmol) with octanal (1 mmol) in the coexistence of 2-octanone (1 mmol) afforded 5-dodecanol, which was an alkylated product of octanal, in 89% yield, and 2-octanone was recovered in essentially quantitative yield. Cyclohexanone and related ketones did not react with n-$Bu_4Pb/TiCl_4$ even at room temperature.

Very high 1.2- and 1.3-asymmetric induction was realized with this reagent (eq 3-5). As shown in eq 3, $Et_4Pb/TiCl_4$ produced high Cram selectivity (93/7) whereas $Et_2Zn/TiCl_4$ gave relatively low selectivity (77/23).[9] The ethylation of 2-benzyloxypropanal with $Et_4Pb/TiCl_4$ gave 2-benzyloxy-3-pentanol in 81% yield along with 7% of the recovered aldehyde. The ratio of chelation/non-chelation product was 98/2 (eq 4). This selectivity was higher than that of the ethylation with EtMgBr. However, other reagents can also produce high diastereoselectivity in 1.2-asymmetric induction of α-oxygen substituted aldehydes,[10] since α-alkoxyaldehydes are an ideal system for chelation control. The ethylation of the β-alkoxyaldehyde gave the adduct in 66% yield along with the recovered aldehyde (24%) (eq 5). The diastereoselectivity with n-$Bu_4Pb/TiCl_4$ was 91/9, and that with n-$Bu_2Zn/TiCl_4$ was 90/10.[11]



(eq 3)

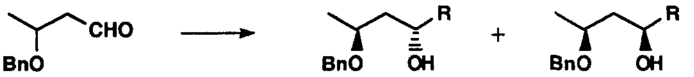
	Cram		anti-Cram
$TiCl_4$ / Et_4Pb -78 → -60°C	93	:	7
$TiCl_4$ / Et_2Zn	77	:	23



(eq 4)

Bn-benzyl

	Chelation		non-Chelation
$TiCl_4$ / Et_4Pb -78 → -60°C	98	:	2
EtMgBr	88	:	12



(eq 5)

	Chelation		non-Chelation
$TiCl_4$ / Et_4Pb -78 → -60°C	78	:	22
$TiCl_4$ / nBu_4Pb -78 → -60°C	91	:	9
nBuMgBr	51	:	49
$TiCl_4$ / Bu_2Zn	90	:	10

As mentioned above, we do not think that RTiLn intervenes as a reactive intermediate. Instead, the aldehyde carbon which is positively charged by coordination of $TiCl_4$ to the oxygen atom may attack the carbon adjacent to Pb (-C-PbR_3) through S_E2 mechanism. However, this does not exclude the possibility of an interaction between R_4Pb and $TiCl_4$. The color of the reaction mixture changed violet when R_4Pb was added to a solution of aldehydes and $TiCl_4$. The violet color must be due to the presence of Ti(III) species, suggesting that charge transfer between $TiCl_4$ and R_4Pb takes place in this three component system. Clearly, further investigation is needed to clarify the reaction mechanism.

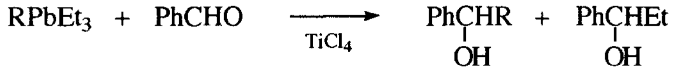
Selective Transfer of One of the Four Alkyl Groups. Only one of the four alkyl groups in R_4Pb can be utilized in the alkylation reaction. To overcome this problem, we investigated the transfer order of alkyl groups in the mixed tetraalkylleads $RPbR'_3$. The results are summarized in Table 2.

Table 2. Transfer Order of $RPbEt_3$ [a]

Isolated Yield, %			Relative Transfer Rate[b]
1 (R)	**2**	**3**	k(R)/K(Et)
Me	62[c]	11	16
Et	96	-	1
iPr	15	71	0.6
nBu	1.7	98	0.06

[a] $RPbEt_3$ was prepared by the reaction of Et_3PbBr with either RMgX or RLi. The transfer order was examined in the reaction of **1** (1.8 mmol) with PhCHO (1 mmol) in the presence of $TiCl_4$ (1.2 mmole) in CH_2Cl_2. [b] The yields of **3** were divided by three. [c] Trace amounts of the chloride, presumably arising from the further chloride substitution reaction of **2**, were formed along with **2**.

The reaction of $RPbEt_3$ (**1**) with benzaldehyde in the presence of $TiCl_4$ gave a mixture of the R-transfer (**2**) and Et-transfer (**3**) products (eq 6). As is obvious from the Table, the transfer order is Me>Et>iPr>nBu. This order is in good agreement with the order of the bromine cleavage of the C-Sn bond of mixed tetraalkyltins.[12] Therefore, the C-C bond formation under the present conditions, R_4Pb-$TiCl_4$, must proceed through an S_E2 process.



$$RPbEt_3 + PhCHO \xrightarrow[TiCl_4]{} \underset{OH}{PhCHR} + \underset{OH}{PhCHEt}$$

(eq 6)

1 2 3

Since it was revealed that the transfer of Bu group was very sluggish, we examined the reactions of Bu_3PbR.[13] The results are summarized in Table 3. Since use of $TiCl_4$ as a Lewis acid caused decomposition of the alkynyltributyllead, $BF_3•OEt_2$ was utilized (entries 1 and 2). The propargyl alcohols were isolated in 64 and 38 % yield, respectively. The rest was the recovered aldehyde. The alkylation proceeded smoothly with $TiCl_4$ (entries 3 and 4). Here again, the starting aldehyde was recovered, but the reaction was relatively clean since it was not accompanied by any side reactions. The reaction of iPr_4Pb with the same aldehyde gave the adduct in 41% yield and thus $iPrPbBu_3$ was superior to iPr_4Pb. Although the vinylation of aldehyde resulted in failure (entry 5), the reaction with the corresponding acetal gave the vinylation product in 37% yield along with the recovered acetal (entry 6).

The reaction of $PhPbBu_3$ with benzaldehyde in the presence of $TiCl_4$ afforded the phenylation-reduction product (57%) along with the recovered aldehyde (eq 7). It is now clear that use of $RPbBu_3$ (R=alkyl, alkynyl, vinyl and aryl) enables the transfer of the R group selectively to electrophiles. This development not only expands a synthetic usefulness of organolead compounds, but also provides a suggestion on the mechanism of R_4Pb-$TiCl_4$ system.

$$PhPbBu_3 + PhCHO \xrightarrow[TiCl_4]{} PhCH_2Ph \qquad \text{(eq 7)}$$

Table 3. Alkynylation, alkylation, and vinylation via $RPbBu_3$[a]

Entry	$RPbBu_3$ R	Electrophile R'CHO	Lewis acid,	Temp. °C	Isolated yield %, RCHR' OH
1	n-Bu-C≡C-	PhCHO	$BF_3•OEt_2$	-78→-30	64
2	n-Bu-C≡C-	n-$C_7H_{15}CHO$	$BF_3•OEt_2$	-78→-30	38
3	iPr	n-$C_7H_{15}CHO$	$TiCl_4$	-78→-30	61
4	Me	n-$C_7H_{15}CHO$	$TiCl_4$	-78→-30	69[b]
5	CH_2=CH-	n-$C_7H_{15}CHO$	$TiCl_4$	-78	trace
6	CH_2=CH-	n-$C_7H_{15}C(OMe)_2$	$TiCl_4$	-78	37

[a] To a CH_2Cl_2 solution of aldehyde (0.5 mmol) and $RPbBu_3$ (1.0~1.2 eq) was added $BF_3•OEt$ (1.2 eq) at -78°C (entries 1 and 2). When $TiCl_4$ was used (entries 3-6), the order of addition was (i) electrophile, (ii) $TiCl_4$, and then (iii) $RPbBu_3$.

[b] Small amounts of chloride (n-$C_7H_{15}CHClMe$) were produced as a by-product.

Experimental Section

Tetraalkyllead compounds were prepared according to the reported procedure.[5]

$$3RM + PbCl_2 + RI \longrightarrow R_4Pb + 2MCl + MI$$

M = Li or MgX

Preparation of Tetraethyllead

Tetraethyllead was prepared by the method described in the literature.[12] To a stirred suspension of 5.6 g (20 mmol) of $PbCl_2$ in 25 ml of dry ether containing 2.6 ml (33 mmol) of EtI was added a solution of EtMgBr, prepared from 6.0 ml (80 mmol) of EtBr and 1.7 g (70 mg atom) of Mg, in 50 ml of dry ether at room temperature. The mixture was refluxed under N_2 for 3 hours. Then, the reaction was treated with H_2O at 0°C. The organic layer was separated and dried over $MgSO_4$. The product was purified by Kugelrohr distillation (82% yield); bp 78°C/10 mmHg.

Preparation of Tetraisopropyllead[5]

To a stirred suspension of 5.6 g (20 mmol) of $PbCl_2$ in 30 ml of dry ether containing 2.5 ml (25 mmol) of iPrI was added a solution of iPrMgBr, prepared from 6.6 ml (70 mmol) of iPrBr and 1.7 g (70 mg atom) of Mg, in 50 ml of dry ether at room temperature. The mixture was refluxed under N_2 for 6 hours. Then, after the usual workup (see Preparation of Tetraethylead), the product was purified by Kugelrohr distillation (66% yield); bp 100°C/5 mmHg.

Preparation of Tetracyclohexyllead[5]

To a stirred suspension of 5.6 g (20 mmol) of $PbCl_2$ in 25 ml or dry ether containing 3.2 ml (25 mmol) of $C_6H_{11}I$ was added a solution of $C_6H_{11}MgBr$, prepared from 6.6 ml (70 mmol) of $C_6H_{11}Br$ and 1.7 g (70 mg atom) of Mg, in 50 ml of dry ether at room temperature. The mixture was refluxed under N_2 for 6 hours. After the usual workup (see Preparation of Tetraethylead), ether was evaporated, and the residue was washed with EtOH. Column chromatography on silica gel (n-hexane) gave the product as white crystals (18 % yield) which decomposed gradually on standing at room temperature.

Preparation of tetrabutyllead[5]

A solution of nBuLi in hexane (1.6 M, 80 mmol) was added to a stirred suspension of 5.56 g (20 mmol) of $PbCl_2$ in 30 ml of dry ether containing 4.0 ml (35 mmol) of BuI at room temperature during 20 minutes. The mixture was stirred at room temperature under N_2 overnight. After the usual workup (see Preparation of Tetraethyllead), the product was purified by Kugelrohr distillation (94% yield); bp 140°C/1 mmHg.

Reaction of R_4Pb with Aldehydes (General Procedure)

All reactions were carried out on 1 mmol scale under argon. The procedure of entry 1 of Table 1 is representative. To a solution of 1 mmol of benzaldehyde in 2 ml of dry CH_2Cl_2 was added at -78°C a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.2 mmol), and then Et_4Pb-CH_2Cl_2 solution (1 M, 1.8 mmol) was added. The mixture was gradually warmed to -30°C. Then, the reaction was treated with aqueous $NaHCO_3$-MeOH. The organic layer was separated and dried over $MgSO_4$. The product was isolated by column chromatography on silica gel (entries 1-3 of Table 1) or on alumina (entries 4-12 of Table 1), by using n-hexane-ether as an eluant. The structures of products were determined by using ^1H-NMR (60 MHz) by comparison with the authentic alcohols which were prepared by reactions of the corresponding aldehydes with either RMgBr or RLi.

Reaction of Et_4Pb with racemic 2-Phenylpropanal

To a solution of 0.13 ml (1 mmol) of 2-phenylpropanal (from Nakarai Chemical Ind.) in 2 ml of dry CH_2Cl_2 was added at -78°C a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.2 mmol), and then Et_4Pb-$TiCl_4$ solution (1 M, 1.3

mmol) was added. The mixture was gradually warmed to -60°C. After the usual workup (see Reaction of R_4Pb with Aldehydes), the products were purified by column chromatography on silica gel (9:1, n-hexane-ether). The retention times of two isomers (the Cram adduct and the anti-Cram adduct) were identical with those of authentic samples which were prepared by the reaction of EtMgBr with 2-phenylpropanal.[13] The product ratio was determined by GLC.

Preparation of 2-Benzyloxypropanal

This aldehyde[14] was prepared from ethyl lactate (Tokyo Kasei Kogyo Co., LTD.) via ethyl 2-benzyloxypropanoate, followed by reduction with LAH, and then Swern oxidation according to the procedure described in the literature.[15]

Reaction of Et_4Pb with 2-Benzyloxypropanal

To a solution of 154.4 mg (0.94 mmol) of 2-benzyloxypropanal in 2 ml of dry CH_2Cl_2 was added a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.1 mmol) at -78°C, and then Et_4Pb-$TiCl_4$ solution (1 M, 2.0 mmol) was added. The mixture was gradually warmed to -60°C. After the usual workup (see Reaction of R_4Pb with Aldehydes), the products were purified by column chromatography on silica gel (9:1, n-hexane-ether). The retention times of two isomers were identical with those of authentic samples which were prepared by the reaction of EtMgBr with 2-benzyloxpropanal.[16] The product ratio was determined by GLC.

Reaction of Et_4Pb with racemic 3-Benzyloxybutanal

3-Benzyloxybutanal was prepared by a modified method of previous literature.[17] To a solution of 170.6 mg (0.96 mmol) of 3-benzyloxybutanal in 2 ml of dry CH_2Cl_2 was added a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.2 mmol), and then Et_4Pb-$TiCl_4$ solution (1 M, 2.0 mmol) was added at -78°C. The mixture was gradually warmed to -60°C. After the usual workup (see Reaction of R_4Pb with Aldehydes), the products were purified by column chromatography on silica gel (9:1, n-hexane-ether). The retention times of two isomers were identical with those of authentic samples which were prepared by the reaction reaction of EtMgBr with 3-benzyloxybutanal[18]. Stereochemical assignment was carried out on the basis of the ^{13}C-NMR (67.5 MHz) spectra. The signals of the carbon atoms bearing the benzyloxy and hydroxyl groups in the major product (δ 72.8 and 69.8, respectively) appear at the relatively higher field in comparison with the corresponding signals of the minor product (δ 76.0 and 73.0, respectively)[11] The product ratio was determined by GLC.

Reaction of n-Bu_4Pb with racemic 3-Benzyloxybutanal

To a solution of 102.6 mg (0.58 mmol) of 3-benzyloxybutanal in 1.2 ml of dry CH_2Cl_2 was added a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 0.7 mmol), and then Et_4Pb-$TiCl_4$ solution (1 M, 1.2 mmol) was added at -78°C. The mixture was gradually warmed to -60°C. After the usual workup (see Reaction of R_4Pb with Aldehydes), purification through a column chromatography on alumina (9:1, n-hexane-ether) followed by silica gel chromatography (benzene) gave the products in 46% yield. Stereochemical assignment and the determination of product ratio were carried out by a similar method described previously.

The major product; ^{13}C-NMR (270MHz) δ 72.8 (C-OBn), 68.5 (C-OH)

The minor product; ^{13}C-NMR (270MHz) δ 76.2 (C-OBn), 71.7 (C-OH)

Preparation of Mixed Tetraalkylleads $RPbR'_3$

Mixed tetraalkylleads were prepared by the reaction of R'_3PbX(X=Br, or Cl) with ether RLi or RMgBr according to the literature.[5]

$$R'_4Pb + Br_2 \longrightarrow R'_3PbBr \xrightarrow[\text{RMgBr}]{\text{RLi or}} R'_3PbR$$

Treatment of Et_4Pb or n-Bu_4Pb with Br_2 gave Et_3PbBr (72%) or n-Bu_3PbBr (74%), respectively. Preparation of mixed tetraalkylleads is summarized in Table 4.

Table 4. Preparation of Mixed Tetraalkylleads

entry	RM	R'_3PbBr	R'_3PbR	yield,%
1	MeLi	Et_3PbBr	Et_3PbMe	81
2	iPrMgBr	Et_3PbBr	Et_3PbiPr	85
3	nBuLi	Et_3PbCl	Et_3PbnBu	92
4	PhLi	Et_3PbBr	Et_3PbPh	87
5	MeLi	nBu_3PbBr	nBu_3PbMe	94
6	iPrMgBr	nBu_3PbBr	nBu_3PbiPr	77
7	PhLi	nBu_3PbBr	nBu_3PbPh	90
8	CH_2=CHMgBr	nBu_3PbBr	nBu_3PbCH=CH_2	91

Preparation of Triethyllead Bromide and Tributyllead Bromide[5]

To a solution of 6.13 g (19 mmol) of Et_4Pb in 75 ml of dry ether was added a solution of 1.1 ml (21 mmol) of Br_2 in 35 ml of dry ether at -70°C. The mixture was gradually warmed to room temperature. Filtration through silica gel layer (ether, then CH_2Cl_2) gave the product. Tributyllead bromide was prepared similarly.

Preparation of Mixed Tetraalkylleads[5]

The procedure of entry 3 of Table 4 is representative. To a solution of 919 mg (2.8 mmol) of Et_3PbCl (from Alfa Products) in 6 ml of dry ether was added a solution of nBuLi in hexane (1.5 M, 3.3 mmol) at -78°C under N_2. The mixture was gradually warmed to 0°C. Then, the reaction was treated with H_2O at 0°C. The organic layer was separated and dried over $MgSO_4$. The product was purified by Kugelrohr distillation, except for nBu_3PbiPr which was purified by column chromatography on silica gel using n-hexane as eluant. A similar procedure was used when R'_3PbBr was reacted with RM.

Et_3PbMe; bp 80°C/16 mmHg. Et_3PbiPr; bp 85°C/5 mmHg

Et_3PbnBu; bp 95°C/5 mmHg. Et_3PbPh; bp 100°C/1 mmHg

nBu_3PbMe; bp 110°C/1 mmHg. nBu_3PbPh; bp 150°C/0.1 mmHg

nBu_3PbCH=CH_2; bp 92°C/0.1 mmHg; ^1H-NMR (270 MHz) δ 7.71 (dd, 1H, J=0.8, 19.7 Hz, $J_{Pb\text{-}c}$ (coupling to ^{207}Pb)=63 Hz), 6.32 (dd, 1H, J=2.3, 9.8 Hz, $J_{Pb\text{-}c}$=91 Hz), 5.67 (dd, 1H, J=2.3, 19.7 Hz, $J_{Pb\text{-}c}$=44 Hz).

Hexynyltriethyllead[19]

A solution of 1.9 g (5 mmol) of Et_3PbBr in 20 ml of dry Et_2O was added to a solution of NaOMe, prepared from 0.14 g (6 mmol) of Na, in 2 ml of dry MeOH at 0°C under N_2. Then, the mixture was stirred at room temperature for 1.5 hours. After the removal of NaBr by using a centrifuge, the solution was concentrated in vacuo. The residue was dissolved in 5 ml of benzene, and 0.98 ml (8.5 mmol) of 1-hexyne was added to this solution. The reaction mixture was stirred at room temperature overnight. The product was purified by Kugelrohr distillation: bp 80-85°C/0.1 mmHg.

Hexynyltributyllead

This compound was prepared by use of the procedure described above employing nBu_3PbBr instead of Et_3PbBr.; 140°C/0.1 mmHg

Reaction of Et_3PbR with Benzaldehyde

The transfer order was examined in the reaction of Et_3PbR (1.8 mmol) with benzaldehyde (1 mmol) in the presence of $TiCl_4$ (1.2 mmol) in dry CH_2Cl_2. The reaction of Et_3PbMe of Table 2 is representative. To a solution of 0.10 ml (1 mmol) of benzaldehyde in 2 ml of dry CH_2Cl_2 was added at -78°C a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.2 mmol), and then a solution of 559 mg (1.8 equiv) of Et_3PbMe in 1 ml of dry CH_2Cl_2 was added. The mixture was gradually warmed to -30°C. After the usual workup (see Reaction of R_4Pb with Benzaldehyde), the product was purified by column chromatography on silica gel (25:1, n-hexane-ethyl acetate then 10:1, n-hexane-ethylacetate). The yields of products were estimated on the basis of the integrated intensities of either ^1H-NMR spectra (90 MHz) or GLC. A small amount of 1-chloroethylbenzene was obtained (about 5%). The yield of this product was counted as a yield of the Me-transfer product.

Preparation of Octyl Aldehyde Dimethyl Acetal

This compound was prepared by the reported procedure.[20] Treatment of octanal (10 mmol) with trimethyl orthoformate (50 mmol) in the presence of a catalytic amount of TsOH gave octanal dimethyl acetal in 93% yield.; ^1H-NMR (270 MHz) δ 4.35 (t, 1H, J=5.5 Hz), 3.32 (s, 6H)

Reaction of $n\text{-}Bu_3PbR$ with Electrophiles

The procedure of entry 1 of Table 3 is representative. To a solution of 0.5 ml (0.5 mmol) of benzaldehyde in 1 ml of dry CH_2Cl_2 was added 0.08 ml (0.6 mmol) of $BF_3{\bullet}Et_2O$ at -78°C, and then a solution of 0.28 g (0.6 mmol) of hexynyltributyllead in 0.5 ml of dry CH_2Cl_2 was added. The mixture was gradually warmed to -30°C, and subsequently the reaction was treated with aqueous $NaHCO_3$. In entries 5 and 6 (Table 3), the reaction was treated with aqueous $NaHCO_3$-MeOH at -78°C after stirring at -78°C for 30 minutes. The organic layer was separated and dried over $MgSO_4$. The product was purified by column chromatography on alumina (n-hexane-ethyl acetate as an eluant). The products were identified by comparing spectroscopically (60 MHz or 90 MHz ^1H-NMR) with the authentic samples which were prepared by reactions of either RMgBr or RLi with the corresponding aldehydes (entries 1-5 of Table 3). When $TiCl_4$ was used (entries 3-6 of Table 3), the order of addition was (i) electrophile, (ii) $TiCl_4$, and then (iii) Bu_3PbR. **3-Methoxy-1-decene**; ^1H-NMR (270 MHz) δ 5.64 (ddd, 1H, J=8, 11, 16 Hz), 5.18 (m, 2H), 3.28 (s, 3H). The ^1H-NMR (60 MHz) spectrum of the product $PhCH_2Ph$ was identical with that of commercially available diphenylmethane (from Tokyo Kasei Kogyo Co., LTD).

Reaction of Hexynyltriethyllead with Benzaldehyde

This reaction was carried out by use of the procedure described in Reaction of Et_3PbR with Benzaldehyde employing $BF_3{\bullet}OEt_2$ instead of $TiCl_4$. In this case, the reaction was stopped at 0°C.

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