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The Formation of Alkyl Acetate in the Reaction of Trialkylborane with Lead(IV) Acetate or Phenyliodoso Acetate*

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In the reaction of trialkylborane with lead(IV) acetate or phenyliodoso acetate in benzene, about two thirds of the alkyl groups of trialkylborane were converted to the corresponding alkyl acetate without any isomerization of the alkyl group. Lead(IV) acetate reacted preferentially with the secondary alkyl group, while phenyliodoso acetate reacted only with the primary alkyl group. In either reaction, one mole of oxidizing agent was consumed for the formation of one mole of alkyl acetate.

Synthetic reactions using organoborane[1)] can be roughly classified into two types by their reaction products.[2)] One is the combination of the alkyl group to the carbon atom, and the other is the combination of the alkyl group to the hetero atom. We are interested in the latter reaction and have studied the severance of the carbon-boron linkage of trialkylborane by oxidation with a metal compound, followed by the combination of the resulting alkyl group with the ligand of the metal compound.

Recently we reported that trialkylborane gave the corresponding alkyl chloride or alkyl bromide in the reaction with aqueous iron(III) chloride[3)] or copper(II) bromide,[3)] and also gave alkyl thiocyanate or alkyl selenocyanate in the reaction with aqueous iron(III) thiocyanate[3,5)] or iron(III) selenocyanate[4,5)] (Eq. 1).

$$R_3B \xrightarrow{Fe^{3+} \text{ or } Cu^{2+},\ X^-} 2RX + RB(OH)_2 \qquad (1)$$

$$X = Cl,\ Br,\ SCN,\ \text{and } SeCN$$

In these reactions, the reduction of Fe(III) to Fe(II) or Cu(II) to Cu(I) occurred; the reactions seemed to proceed in ligand-transfer oxidation by metal compounds for the alkyl radical generated from trialkylborane.[6)]

Kochi described that the oxidation of alkyl radical by copper(II) acetate and lead(IV) acetate involved an electron-transfer mechanism, and now, by the former reagent,[7)] olefin was formed as the major product by the elimination of hydrogen from the alkyl radical, while by the latter reagent, substitution product,[8)] RX (X=H, OAc, and R′, derived from the solvent) was characteristically produced.

On the other hand, Suzuki and his co-workers[9)] found that alkyl acetate was formed by an anodic oxidation of trialkylborane in an acetic acid–sodium acetate solution.

Thus, we studied the reaction of trialkylborane with lead(IV) acetate in the hope that alkyl acetate might be formed from trialkylborane.

Results and Discussion

Reaction of Trialkylboranes with Lead(IV) Acetate. As a preliminary examination, trihexylborane, prepared by the hydroboration of 1-hexene with borane in tetrahydrofuran, was subjected to a reaction with the benzene solution of lead(IV) acetate. A relatively slow reaction occurred. The reaction mixture was worked up, and then distilled to give two compounds in a ratio of 10 : 1. These compounds were identified as hexyl acetate (the major one) and 1-methylpentyl acetate (the minor one) by direct comparisons with authentic samples. When the tetrahydrofuran was taken off before the addition of lead(IV) acetate, the amount of hexyl acetates increased remarkably. Accordingly, the subsequent reactions were conducted in the absence of tetrahydrofuran.

To obtain optimum reaction conditions, the reaction was carried out using varying amounts of lead(IV) acetate under several temperatures. Some results are presented in Table 1.

In the reaction at 55 °C for 24 h, the best results were obtained giving 7.8 mmol of hexyl acetate and 0.8 mmol of 1-methylpentyl acetate from 5 mmol of trihexylborane. On the oxidation of the reaction mixture with an aqueous hydrogen peroxide solution, under weakly basic conditions, 7.8 mmol of hexyl acetate, 0.8 mmol of 1-methylpentyl acetate, 6.3 mmol of hexyl alcohol, and a trace amount of 1-methylpentyl alcohol were obtained. A characteristic feature of the reaction is revealed by these results. That is, two thirds of the alkyl group of trialkylborane can participate in the reaction, giving alkyl acetate almost exclusively, without any isomerization of the alkyl group. This characteristic is worthy of remark because, in the reaction of valeric acid with the lead(IV) acetate butyl

TABLE 1. REACTION[a)] OF TRIHEXYLBORANE WITH LEAD(IV) ACETATE

Exp. no.	React. temp, °C	$Pb(OAc)_4$ mmol	Products, mmol[b)] Hexyl acetate	1-Methylpentyl acetate
1	20	15	0.8	0.3
2	40	15	5.5	0.6
3	55	15	7.8	0.8
4	75	15	6.0	0.8
5	55	10	7.2	0.8
6	55	5	4.7	0.3
7	55	2.5	2.2	0.2

a) The reaction was carried out in benzene for 24 h by using 5 mmol of trihexylborane, prepared from 1-hexene by hydroboration. b) Determined by GLPC, using PEG 20 M as the liquid phase.

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$$\text{Valeric acid} \xrightarrow[\text{benzene}]{Pb(OAc)_4} \underset{25\%}{\text{butane}} + \underset{2\%}{\text{1-butene}} + \underset{1.1\%}{\text{2-butene}}$$
$$+ \underset{20.6\%}{\text{butylbenzene}} + \underset{2\%}{\text{butyl acetate}}$$
$$+ \underset{2\%}{\text{1-methylpropyl acetate}}$$

Scheme 1.

radical, initially formed by decarboxylation, several reaction products were given by electron-transfer oxidation[8] (Scheme 1). In the present reaction, only trace amounts of hexane, hexene, and hexylbenzene were detected.

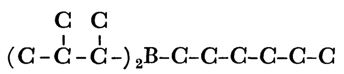
As is shown in Exp. 6 and 7, one mole of lead(IV) acetate is consumed in the formation of one mole of hexyl acetate, suggesting that two electrons take part in the formation of one molecule of hexyl acetate. Thus, the reaction may be written stoichiometrically as follows:

$$R_3B + 2Pb(OAc)_4 \longrightarrow 2\ ROAc + RB(OAc)_2 + 2Pb(OAc)_2. \quad (2)$$

The results of the reactions of several trialkylboranes with lead(IV) acetate under the optimum reaction conditions are presented in Table 2.

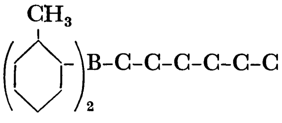
Similar results were obtained in all the reactions examined. For example, 5 mmol of tri-*exo*-2-norbornylborane gave 8.5 mmol of *exo*-2-norbornyl acetate.

Another important feature of the reaction is the fact that the secondary alkyl group reacts in preference to the primary one in the case of the mixed trialkylborane, which contains primary and secondary alkyl groups on the same boron atom. That is, dicyclohexylhexylborane gave mostly cyclohexyl acetate. Further, although one third of the hexyl group still remained on the boron atom, almost all of the 1-methylpentyl group[10] was converted to 1-methylpentyl acetate in the reaction of trihexylborane. Bis(1,2-dimethylpropyl)hexylborane (**1**) and bis(2-methylcyclohexyl)hexylborane (**2**) gave only trace amounts of products, and, on oxidation with an aqueous hydrogen peroxide solution, under weakly basic conditions, the corresponding alcohols were formed quantitatively. Although, in both cases, no detailed study has been made, the large steric hindrance on the boron atom seems to prevent any interaction between trialkylborane and lead(IV) acetate.



$$(C-\overset{C}{\underset{|}{C}}-\overset{C}{\underset{|}{C}}-)_2B-C-C-C-C-C-C$$

(**1**)



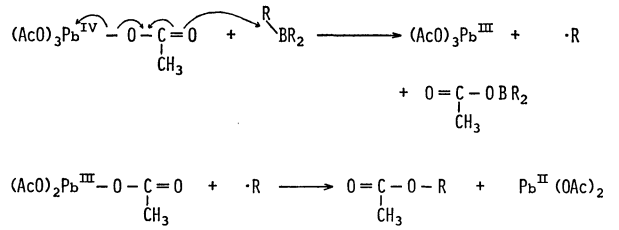
(**2**)

When 5 mmol of tricyclohexylborane was allowed to react with lead(IV) acetate in chloroform, 1.6 mmol of cyclohexyl acetate and 2.2 mmol of cyclohexyl chloride were formed. This fact strongly suggests that an alkyl radical has an important role in the reaction. Although describing the reaction mechanism in detail is not the main purpose of this report, these results may be explained by the following reaction scheme:

Table 2. Reaction[a)] of trialkylboranes with lead(IV) acetate

R_3B (5 mmol)	Product	Yield,[b)] mmol
(1-Me-propyl)$_3$B	1-Me-propyl-OAc	7.5
(Hexyl)$_3$B	Hexyl-OAc 1-Me-pentyl-OAc	7.8 (7.5)[c)] 0.8 (0.7)[c)]
(Cyclohexyl)$_3$B	Cyclohexyl-OAc	7.7 (7.1)[c)]
(Octyl)$_3$B	Octyl-OAc 1-Me-heptyl-OAc	5.7 (5.5)[c)] 0.6 (0.5)[c)]
(Cyclooctyl)$_3$B	Cyclooctyl-OAc	6.0 (6.0)[c)]
(Norbornyl)$_3$B	*exo*-Norbornyl-OAc	8.5 (8.4)[c)]
(Cyclohexyl)$_2$B-hexyl	Cyclohexyl-OAc Hexyl-OAc	6.2 0.5

a) Carried out at 55 °C for 24 h by using 15 mmol of Pb(OAc)$_4$ and 25 ml of benzene. b) Determined by GLPC. c) Isolated by distillation.



Scheme 2.

Many reactions of organoborane with oxidizing agents have been studied, and in many cases characteristic products for each reaction have been obtained.[11-14] The present reaction gave alkyl acetate characteristically. On the other hand, synthetic methods of alkyl carboxylate from olefin have also been reported.[9,15] Except for the reaction cited in Ref. 9, though, they are all "Markownikoff addition" reactions of carboxylic acid to olefin. The present reaction is a practically applicable one-pot synthesis of primary alkyl acetate from α-olefin by means of the "Anti-Markownikoff addition" reaction.

Reaction of Trialkylborane with Phenyliodoso Acetate. Next, we examined the reaction of trialkylborane with phenyliodoso acetate, which is known to act in almost the same manner as lead(IV) acetate in oxidation reactions.[16] The results are presented in Table 3.

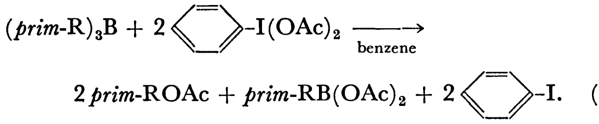
In contrast to the oxidation with lead(IV) acetate, phenyliodoso acetate converted only the primary alkyl group to primary alkyl acetate. For example, 5 mmol of dicyclohexylhexylborane gave only 4.4 mmol of hexyl acetate; on the oxidation of the reaction mixture with the aqueous hydrogen peroxide solution, under weakly basic conditions, 4.4 mmol of hexyl acetate, 10 mmol of cyclohexyl alcohol, and 0.4 mmol of hexyl alcohol were obtained. In the case of trihexylborane, hexyl acetate was formed, uncontaminated with 1-methylpentyl acetate. Thus, the reaction provides a more excellent method than that of lead(IV) acetate for the synthesis of primary alkyl acetate from α-olefin.

TABLE 3. REACTION[a)] OF TRIALKYLBORANES WITH PHENYLIODOSO ACETATE

R_3B (5 mmol)	Product	Yield,[b)] mmol
$(\text{Hexyl})_3B$	Hexyl-OAc	9.3 (9.2)[e)]
	1-Me-pentyl-OAc	trace (trace)[e)]
	Hexyl-OAc	4.5[c)]
		2.4[d)]
$(\text{Cyclohexyl})_3B$	Cyclohexyl-OAc	no reaction
$(\text{Octyl})_3B$	Octyl-OAc	7.2 (7.0)[e)]
	1-Me-heptyl-OAc	trace (trace)[e)]
$(\text{Cyclohexyl})_2B$-hexyl	Hexyl-OAc	4.4
	Cyclohexyl-OAc	0

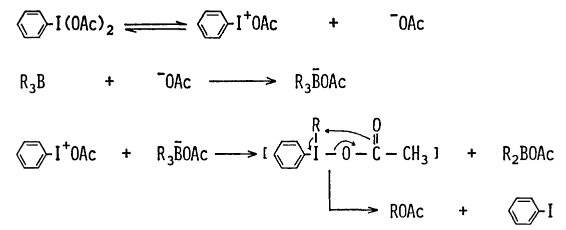
a) Carried out at 55 °C for 8 h by using 10 mmol of phenyliodoso acetate and 20 ml of benzene. b) Determined by GLPC. c) Phenyliodoso acetate, 5 mmol. d) Phenyliodoso acetate, 2.5 mmol. e) Isolated by column chromatography.

As has been shown in the reaction of trihexylborane, one mole of phenyliodoso acetate was consumed for the formation of one mole of hexyl acetate, and a comparable amount of iodobenzene was formed (Eq. 3):



(3)

The yield of alkyl acetate was not reduced in the presence of tetrahydrofuran. Moreover, no alkyl chloride was formed in the reaction conducted in chloroform. These facts seem to show that, in contrast to the case of lead(IV) acetate, the alkyl radical is not involved in the reaction. Pelter et al. described that, in the nucleophilic migration of the alkyl group of the trialkylborane cyanate complex, the primary alkyl group is more labile than the secondary one.[17)] Thus, in the reaction of trialkylboranes with phenyliodoso acetate, it is probable that the nucleophilic attack of the alkyl group on the iodonium cation is involved. The following reaction scheme may be proposed:



Scheme 3.

As has been described previously, lead(IV) acetate converts preferentially the secondary alkyl group, while phenyliodoso acetate converts only the primary one. Thus, both reactions, compensating for each other, may provide a new method of synthesizing alkyl acetates from a variety of olefins.

Experimental

Instruments. GLPC was performed using a NEVA Model 1400. The PMR spectra were obtained on a Hitachi Model R-20A spectrometer. The infrared spectra were recorded on a Shimadzu 27G spectrometer. The mass spectra were obtained on a Hitachi Model M-52 mass spectrometer.

Materials. Commercial 1-hexene, 1-octene, cyclohexene, cyclooctene, benzene, and tetrahydrofuran were dried with lithium aluminium hydride and used after distillation under an argon atmosphere. Commercial 2-norbornene and 2-butene were used without any purification. The chloroform was dried over phosphorus pentaoxide and was used after distillation under an argon atmosphere.

The tetrahydrofuran solution of borane was prepared by the method described in the literature.[11)]

The lead(IV) acetate was prepared by the method described in the literature,[18)] its purity was above 98%.[19)]

The phenyliodoso acetate was prepared by the method described in the literature;[20)] mp 157—158 °C (lit, 158 °C).

Reaction of Trialkylborane with Lead(IV) Acetate. The following procedure is representative. A dry, 50-ml, round-bottomed flask, equipped with a gas inlet, a magnetic stirring bar, a septum inlet, a reflux condenser, and a dropping funnel, was flushed with argon. In the flask 5.63 ml (15 mmol) of 1-hexene was hydroborated with 5 mmol of borane in tetrahydrofuran, and then the tetrahydrofuran was removed under reduced pressure at 40 °C. In an argon atmosphere, 6.65 g (15 mmol) of lead(IV) acetate in 25 ml of benzene was added, drop by drop, to the trihexylborane through the dropping funnel, after which the solution was stirred at 55 °C for 24 h. The lead(II) acetate was precipitated as a white solid with the progress of reaction. In the analytical experiment, the solution, to which an internal standard substance has been added, was analysed by GLPC (PEG 20M, supported on Diasolid M, was used as the liquid phase). In the preparative experiment, 10 ml of water was added to the solution to destroy any residual lead(IV) acetate. Then the mixture was saturated with sodium chloride, and the lower aqueous layer was separated and extracted with pentane several times. The combined upper organic layer and pentane extracts were washed with a saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. On distillation at 170 °C/757 mmHg, 1.15 g of a mixture containing 7.5 mmol of hexyl acetate and 0.7 mmol of 1-methylpentyl acetate was obtained. The IR, PMR, and mass spectra of all the alkyl acetates, except for norbornyl acetate, were consistent with those obtained from authentic samples.

exo-*2-Norbornyl Acetate*: The IR spectrum showed a strong band at 1730 cm^{-1}. The mass spectrum (20 eV) was completely consistent with the standard spectrum[21)] of 2-norbornyl acetate ($m/e=154$, M^+). PMR (CCl_4, TMS) spectrum; $\delta=0.95-1.95$ (m, 4H, H-3,5,6,7), 1.88 (s, 3H), 2.24 (br, s, 2H, H-1,4), 4.48 (dd, 2H, $J_{\text{H-2 }endo\text{-H-3 }exo}=2$ Hz and $J_{\text{H-2 }endo\text{-H-3 }endo}=9$ Hz.)

Reactions of Trialkylboranes with Phenyliodoso Acetate. To trialkylborane, prepared in the same manner as in the reaction with lead(IV) acetate, a 3.22-g portion (10 mmol) of phenyliodoso acetate in 20 ml of benzene was added, drop by drop, after which the mixture was stirred at 55 °C for 8 h. A yellowish homogeneous solution resulted. In the analytical experiment, the solution, into which an internal standard substance has been added, was analysed by GLPC (PEG 20M, supported on Diasolid M, was used as the liquid phase). In the preparative experiment, the solvent was removed under reduced pressure and the products were separated by column chromatography (silica gel). Iodobenzene, formed by the reduction of phenyliodoso acetate, was effectively removed by elution with hexane, and then the alkyl acetate was eluted with benzene.

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