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PREPARATION OF MIXED DIORGANOTHALLIUM(III) ISOBUTYRATES AND THEIR REPLACEMENT REACTION WITH TETRAMETHYLTIN

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SUMMARY

Various mixed diorganothallium isobutyrates were prepared. A novel replacement reaction was observed by treating them with tetramethyltin in methanol as follows,

$$\mathrm{RR'TlOCOC_3H_7\text{-}iso + (CH_3)_4Sn + CH_3OH \rightarrow CH_3RTlY' + (CH_3)_3SnY' + R'H}$$
$$\mathrm{(Y' = OCOC_3H_7\text{-}iso\ and/or\ OCH_3)}$$

where R′ is evidently limited to groups in which the carbon atom bonded to thallium has *sp* or sp^2 hybridization.

We have briefly reported[1] the preparation of mixed diorganothallium(III) chlorides by the reaction of monoorganothallium diisobutyrates[2] with tetramethyltin or phenylboronic acid, followed by addition of hydrochloric acid. Similar reactions are found to proceed smoothly and nearly quantitatively as shown in eqns. (1) and (2).

$$\mathrm{RTlY_2 + (CH_3)_4Sn \rightarrow CH_3RTlY + (CH_3)_3SnY} \tag{1}$$
$$\mathrm{RTlY_2 + R'B(OH)_2 \rightarrow RR'TlY} \tag{2}$$
$$\mathrm{(R = CH_3, C_2H_5, n\text{-}C_3H_7\ and\ C_6H_5; R' = C_6H_5\ and\ }p\mathrm{\text{-}CH_3\text{–}C_6H_4}$$
$$\mathrm{Y = OCOC_3H_7\text{-}iso)}$$

We have also found that monomethylthallium diisobutyrate reacts with other tetraalkyltins.

$$\mathrm{CH_3TlY_2 + R_4Sn \rightarrow CH_3RTlY + R_3SnY} \tag{1'}$$
$$\mathrm{(R = C_2H_5, n\text{-}C_3H_7\ and\ CH_2{=}CH; Y = OCOC_3H_7\text{-}iso)}$$

The reaction with either tetraethyl- or tetra-n-propyltin was slow, and the product was contaminated by a dimethylthallium species. It is not yet clear whether this species was formed from the disproportionation of $\mathrm{CH_3TlY_2}$ or $\mathrm{CH_3RTlY}$. However, with the exception of these two cases, the alkylation reaction proceeds straightforwardly as shown in (1) and (1′). This is noteworthy in view of the report[3] that phenylthallium dichloride reacts with alkyl Grignard reagents to give a mixture of diphenylthallium halide and the corresponding dialkylthallium halide.

Tetramethyltin also reacts with various mixed diorganothallium isobutyrates, causing a novel replacement reaction as shown in eqn. (3)

$$\mathrm{RR'TlY + (CH_3)_4Sn + CH_3OH \rightarrow CH_3RTlY' + (CH_3)_3SnY' + R'H} \quad (3)$$

$$\mathrm{R = CH_3\ and\ C_2H_5; R' = C_6H_5,}\ p\text{-}\mathrm{CH_3{-}C_6H_4, C_6H_5C{\equiv}C\ and}$$
$$\mathrm{CH_2{=}CH; Y = OCOC_3H_7\text{-}iso; Y' = OCOC_3H_7\text{-}iso\ and/or\ OCH_3)}$$

This reaction proceeds smoothly, and methanol is thought to act as a proton source for the formation of the hydrocarbons (R'H)[*]. It should be noted that methylethylthallium isobutyrate does not undergo this reaction, *i.e.* the organic group (R') is replaced only when the carbon atom bonded to thallium has *sp* or sp^2 hybridization.

Presumably this reaction does not proceed by way of a simple R'-methyl exchange mechanism. In that event the reaction of $\mathrm{R(C_6H_5)TlY}$ with $\mathrm{(CH_3)_4Sn}$ would give the intermediate $\mathrm{(CH_3)_3(C_6H_5)Sn}$, but this compound is found to be unreactive toward methanol under the reaction conditions employed. A likely mechanism may involve isobutyryloxy–methyl exchange, and the resulting $\mathrm{CH_3RR'Tl}$ could then react with methanol to lose only the most electronegative R' group, preferentially forming R'H before the disproportionation of $\mathrm{CH_3RR'Tl}$ takes place.

$$\mathrm{RR'TlY + (CH_3)_4Sn \rightarrow CH_3RR'Tl + (CH_3)_3SnY}$$
$$\mathrm{CH_3RR'Tl + CH_3OH \rightarrow CH_3RTlOCH_3 + R'H}$$

However, such a disproportionation reaction through intermolecular exchange of alkyl groups has been reported to occur very rapidly in mixed tri(methyl, ethyl)-thallium and tri(methyl, vinyl)thallium systems[4]. Alternatively, it is also possible that the methylation by tetramethyltin and the cleavage of the Tl–R' bond take place simultaneously in the sense of a concerted mechanism, without formation of a $\mathrm{CH_3}$-RR'Tl intermediate.

EXPERIMENTAL

Starting materials

n-Propylthallium diisobutyrate was prepared in a similar manner reported for methyl- and ethylthallium diisobutyrates[2]. White, fluffy crystals were recrystallized from chloroform and acetone (62%); m.p. 124–125° (decompn.). (Found: C, 31.69; H, 5.24; Tl, 48.10. $\mathrm{C_{11}H_{21}O_4Tl}$ calcd.: C, 31.33; H, 5.02; Tl, 48.47%.) Trimethylphenyltin was prepared according to a described method[5].

Preparation of $\mathrm{RR'TlOCOC_3H_7}$-iso

The properties and analytical data of the mixed diorganothallium isobutyrates prepared in this work are summarized in Table 1. These mixed diorganothallium isobutyrates were prepared from the reaction of the corresponding chlorides[1] with thallous isobutyrate in methanol. It is also possible to prepare them by the following methods.

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[*] The reaction of ethylphenylthallium isobutyrate and tetramethyltin in methylene chloride or chloroform does not proceed under the reaction conditions employed.

TABLE 1

PROPERTIES OF $RR'TlOCOC_3H_7$-iso

Method of prepn.	Compound		M.p. (°C) (decompn.)	Analysis found (calcd.) (%)		
	R	R'		C	H	Tl
(1), (1')	CH_3	C_2H_5	238–239	25.05 (25.06)	4.37 (4.51)	61.10 (60.90)
(1), (1')	CH_3	n-C_3H_7	213	27.71 (27.49)	5.00 (4.90)	
(1), (2)	CH_3	C_6H_5	210–211	34.54 (34.44)	3.81 (3.94)	
(2)	CH_3	p-CH_3-C_6H_4	218–220	36.11 (36.25)	4.62 (4.31)	
(1')	CH_3	CH_2=CH	206–206.5	25.09 (25.21)	4.07 (3.93)	61.07 (61.27)
(2)	C_2H_5	C_6H_5	211–211.5	36.70 (36.25)	4.46 (4.31)	
(2)	C_2H_5	p-CH_3-C_6H_4	212	37.81 (37.93)	4.56 (4.65)	

Methylethylthallium isobutyrate, $CH_3(C_2H_5)TlOCOC_3H_7$-iso; reaction (1). Ethylthallium diisobutyrate (4 g; 10 mmoles) and tetramethyltin (1.8 g; 10 mmoles) were dissolved in 50 ml of dry methanol and kept for 3 h at room temperature. After evaporating the solution, 300 ml of ether was added to the residual solid and the soluble trimethyltin isobutyrate was separated by filtration. The remaining white solid was recrystallized from methanol and acetone to give 2.7 g (81%) of methylethylthallium isobutyrate.

Methylphenylthallium isobutyrate, $CH_3(C_6H_5)TlOCOC_3H_7$-iso; reaction (2). Methylthallium diisobutyrate (3.9 g; 10 mmoles) and phenylboronic acid (1.5 g; 12 mmoles) were dissolved in 30 ml of methanol and kept for 5 h. Adding water together with a drop of isobutyric acid gave a white precipitate, which was filtered and recrystallized from methanol and water to give $CH_3(C_6H_5)TlOCOC_3H_7$-iso (2.8 g; 74%).

Reaction of $CH_3Tl(OCOC_3H_7\text{-iso})_2$ with $(C_2H_5)_4Sn$; reaction (1'). Methylthallium diisobutyrate (0.4 g; 1 mmole) and tetraethyltin (0.45 g; 2 mmole) were dissolved in chloroform (10 ml) and kept for two days. An excess of an aqueous KCl solution was added to give white crystals, which were separated and recrystallized from pyridine to give 0.15 g of a mixture of $CH_3(C_2H_5)TlCl$ (ref. 1) and $(CH_3)_2TlCl$, whose IR spectra are the same as those of authentic samples.

Alkyl replacement reaction of $RR'TlOCOC_3H_7$-iso; reaction (3)

The reaction was carried out in a tube and was followed by PMR spectroscopy. The reaction conditions and the yield, calculated from the relative intensities of the methyl signals of the organothallium compounds, are shown in Table 2.

By treating the reaction mixture with an excess of an aqueous KCl solution, the organothallium compounds were derivatized to $(CH_3)_2TlCl$ and $CH_3(C_2H_5)$-$TlCl$ and identified by IR spectra. Ethylene was identified by gas-chromatography analysis carried out on a Hitachi K-23 using a column packed with active carbon at 140°. Benzene, toluene and phenylacetylene were analyzed gas-chromatographically

TABLE 2

REACTIONS OF RR'TlOCOC$_3$H$_7$-iso WITH (CH$_3$)$_4$Sn IN CH$_3$OH[a]

RR'TlOCOC$_3$H$_7$-iso			(CH$_3$)$_4$Sn (mmole)	Time (days)	Temp. (°C)	Yield[b] (%)
R	R'	(mmole)				
CH$_3$	C$_6$H$_5$	0.2	0.55	8	r.t.	35
CH$_3$	p-CH$_3$-C$_6$H$_4$	0.2	0.55	8	r.t.	35
CH$_3$	C$_6$H$_5$C≡C[c]	0.2	0.25	1	r.t.	100
CH$_3$	CH$_2$=CH	0.2	0.53	3	60	100
C$_2$H$_5$	C$_6$H$_5$	0.2	0.8	8	r.t.	[d]
C$_2$H$_5$	p-CH$_3$-C$_6$H$_4$	0.2	0.3	3	60	65

[a] Conc. 10–17 wt.% for thallium compounds. [b] Calculated from the relative intensities of the methyl signals of thallium compounds. [c] CH$_3$(C$_6$H$_5$C≡C)TlOAc (ref. 6) was used. [d] Almost quantitative (by the disappearance of the peaks due to C$_2$H$_5$(C$_6$H$_5$)TlOCOC$_3$H$_7$-iso).

with a Yanagimoto GCG-3 using a column packed with DNP at 88° and/or 130°. Typical reactions are as follows.

(*i*). *Ethylphenylthallium isobutyrate,* $C_2H_5(C_6H_5)TlOCOC_3H_7$*-iso.* Ethylphenylthallium isobutyrate (0.08 g; 0.2 mmole) and tetramethyltin (0.152 g; 0.8 mmole) were dissolved in dry methanol (0.476 g) and kept for 8 days at room temperature. The results of PMR measurements before and after the reaction are shown in Fig. 1. The peaks due to ethylphenylthallium isobutyrate disappeared and were replaced by

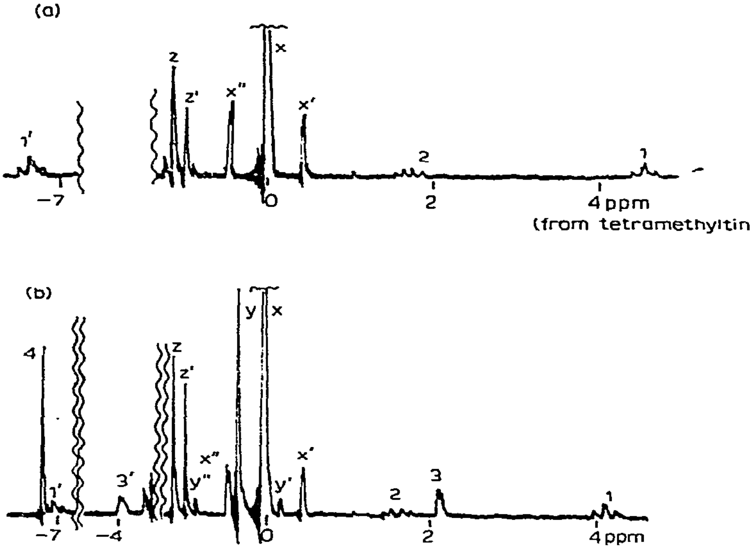

Fig. 1. Proton magnetic resonance spectra for the reaction of C$_2$H$_5$(C$_6$H$_5$)TlOCOC$_3$H$_7$-iso and (CH$_3$)$_4$Sn in CH$_3$OH.

(a) The spectrum before the reaction. C$_2$H$_5$(C$_6$H$_5$)TlOCOC$_3$H$_7$-iso: 1 1', CH$_3$(CH$_2$); 2, (CH$_3$)CH$_2$; z z', OCOC(CH$_3$)$_2$. (CH$_3$)$_4$Sn: x x' x'', CH$_3$.

(b) The spectrum after the reaction. CH$_3$(C$_2$H$_5$)TlY': 1 1', CH$_3$(CH$_2$); 2, (CH$_3$)CH$_2$; 3 3', CH$_3$; z z', OCOC(CH$_3$)$_2$. Benzene: 4, C$_6$H$_6$. (CH$_3$)$_4$Sn: x x' x'', CH$_3$. (CH$_3$)$_3$SnY': y y' y'', CH$_3$. (Y' = OCOC$_3$H$_7$-iso and/or OCH$_3$).

those attributed to trimethyltin and methylethylthallium moieties as well as benzene. The distillate of the reaction mixture contained methanol, residual tetramethyltin and benzene, which were identified gas-chromatographically.

(*ii*). *Methylvinylthallium isobutyrate*, $CH_3(CH_2{=}CH)TlOCOC_3H_7$-*iso*. Methylvinylthallium isobutyrate (0.067 g; 0.2 mmole) and tetramethyltin (0.12 g; 0.53 mmole) were dissolved in dry methanol (0.538 g) and kept for 3 days at 60°. Examination of the PMR spectra before and after the reaction showed the disappearance of the peak (at 2.76 ppm from tetramethyltin) which was the higher field signal of the doublet of the methyl protons of methylvinylthallium isobutyrate. The spectrum after the reaction was the same as that of a mixture of dimethylthallium hydroxide, trimethyltin isobutyrate and tetramethyltin in methanol, except for an additional singlet peak at −5.26 ppm from tetramethyltin. This peak disappeared after repeated evacuation of the tube and was assigned to the proton signal of ethylene. The vapor phase of the reaction mixture contained ethylene and residual tetramethyltin, which were also detected by gas-chromatography.

In order to clarify the mechanism, an equimolar amount of trimethylphenyltin and dimethylthallium isobutyrate were dissolved in methanol and kept for a week. No change was observed in the PMR spectra of this mixture.

IR and PMR spectra

The IR spectra in nujol mulls were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings. The PMR spectra were obtained using a Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz and 20°.

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