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PREPARATION AND REACTIONS OF METHYL(ALLYL)THALLIUM(III) DERIVATIVES

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SUMMARY

Several methyl(allyl)thallium derivatives have been prepared for the first time. The IR and PMR spectra of these compounds indicate the presence of σ-allyl–thallium bonds. In the cleavage reactions of these compounds with tetramethyltin in methanol or with metal salts such as $Hg(OCOCH_3)_2$, PdX_2 ($X = OCOC_2H_5$ and Cl) and $RhCl_3 \cdot 3H_2O$, preferential cleavage of the allyl–thallium bond occurs to give propylene in the case of tetramethyltin and allylic derivatives of the metals in the other cases.

INTRODUCTION

In the course of our studies[1,2] on the reactions of mixed diorganothallium compounds, we have prepared a series of new methyl(allyl)thallium derivatives. Allylthallium compounds have not been reported previously, and it seemed of interest to determine whether the allyl–thallium bond is in dynamic equilibrium, as often found in allylic derivatives of Mg[3], Zn[4], Cd[5] and B[6], or is "frozen" as is the case in derivatives of Hg[7] and the Group IV elements[8].

In the novel replacement reaction[1] of some mixed diorganothallium compounds, RR′TlY, with tetramethyltin in methanol, it had been observed that an organic group R′ is replaced smoothly to produce the hydrocarbon R′H only when the carbon atom bonded to thallium has *sp* or *sp*^{2} hybridization. However, an extension of this reaction to these new methyl(allyl)thallium compounds shows that the allyl group is also prone to this type of replacement. We also report Tl–allyl cleavage in reactions of these compounds with some metal (Hg^{II}, Pd^{II} and Rh^{III}) salts.

DISCUSSION

Methyl(allyl)thallium carboxylates were obtained in moderate yields from the following reactions (under mild conditions) of monomethylthallium compounds with tri-n-butyl(allyl)tin[9].

$$CH_3Tl(CN)OCOCH_3 + (n\text{-}C_4H_9)_3SnC_3H_5 \rightarrow CH_3(C_3H_5)TlOCOCH_3 + (n\text{-}C_4H_9)_3SnCN$$

$$\begin{aligned} &CH_3Tl(OCO\text{-}i\text{-}C_3H_7)_2+(n\text{-}C_4H_9)_3SnC_3H_5 \rightarrow \\ &\qquad CH_3(C_3H_5)TlOCO\text{-}i\text{-}C_3H_7+(n\text{-}C_4H_9)_3SnOCO\text{-}i\text{-}C_3H_7 \end{aligned}$$

The carboxylates can be derivatized to $CH_3(C_3H_5)TlY$ using appropriate reagents, HY or KY ($Y=Cl$, $SSCN(CH_3)_2$, $OCOC_2H_5$ and tropolonate).

The infrared spectra of all of these methyl(allyl)thallium compounds in both the solid state and in solution show the characteristic bands due to the terminal vinyl group, except where obscured by absorption due to the ligand Y (see Table 2). These bands are similar to those observed for the σ-allyl–metal compounds, C_3H_5HgX[7] and $(C_3H_5)_nSnR_{4-n}$[10].

The PMR spectra of these methyl(allyl)thallium derivatives also indicate the presence of the so-called frozen σ-allyl group at room temperature, and thallium–proton spin-spin couplings were observed clearly (Fig. 1 and Table 3). When compared to the other compounds, methyl(allyl)thallium dithiocarbamate displays smaller $J(Tl\text{–}CH_3)$ and $J(Tl\text{–}CH_2\text{–})$ values and also a lower $\nu_{asym}(Tl\text{–}C)$ frequency. This may be suggestive of weaker Tl–C bonds in the dithiocarbamate, as was reported to be the case in other diorganothallium dithiocarbamates[2]. The fact that the $J(Tl\text{–}CH_3)$ values for methyl(allyl)thallium derivatives, $CH_3(C_3H_5)TlY$, are smaller than those for the corresponding dimethylthallium compounds[11], $(CH_3)_2TlY$, may be interpreted in terms of the more electropositive character of the allyl group as compared to the methyl group, based on the proposed theory of Bent[12] as in the case of organotin compounds[13].

As shown in equation (1), it has now been found that in the reaction of methyl(allyl)thallium acetate with tetramethyltin in methanol, the more electropositive allyl group is cleaved to give a dimethylthallium species and propylene together with a trimethyltin species. This result contrasts with our earlier study[1] of this reaction with other diorganothallium compounds, in which it was observed that cleavage of an organic group occurred only when the carbon atom bonded to thallium had sp or sp^2 hybridization. Methyl(allyl)thallium acetate also reacts with mercuric acetate, as shown in (2) where $R=CH_3$ and $R'=C_3H_5$, to give acetates of monomethylthallium and allylic mercury, while in the reactions of other mixed diorganothallium acetates with mercuric acetate the more electronegative substituent is transferred to mercury, as shown in (2) where $R=CH_3$, $R'=C_6H_5$; $R=CH_3$, $R'=CN$ or $R=C_2H_5$, $R'=CH_3$.

$$\begin{aligned} &CH_3(C_3H_5)TlOCOCH_3+(CH_3)_4Sn \xrightarrow{CH_3OH} \\ &\qquad (CH_3)_2TlY+(CH_3)_3SnY+CH_3CH{=}CH_2 \qquad (1) \\ &(Y=OCOCH_3 \text{ and/or } OCH_3) \end{aligned}$$

$$\begin{aligned} &RR'TlOCOCH_3+Hg(OCOCH_3)_2 \xrightarrow{CH_3OH} \\ &\qquad RTl(OCOCH_3)_2+R'HgOCOCH_3 \qquad (2) \end{aligned}$$

$$\begin{aligned} &CH_3(C_3H_5)TlY+PdY_2 \xrightarrow{CH_2Cl_2} CH_3TlY_2+0.5\,(\pi\text{-}C_3H_5PdY)_2 \qquad (3) \\ &(Y=OCOC_2H_5) \end{aligned}$$

The reaction with palladous propionate proceeds as shown in (3), but in the reactions with $PdCl_2$ and $PdCl_2\cdot 2C_6H_5CN$, the monomethylthallium species decomposed to give CH_3Cl and $TlOCOCH_3$. On the other hand, an unexpected product, $(CH_3)_2TlCl$, in addition to TlCl was obtained in the reaction with $RhCl_3 \cdot 3H_2O$.

It is possible that the preferential cleavage of the allyl–thallium bond in these reactions may be due to a specific interaction between the π-electron system and an electrophilic reagent, such as the proton in (1) or a metal cation in (2) (where $R = CH_3$ and $R' = C_3H_5$) or (3).

EXPERIMENTAL

Preparations

Methyl(allyl)thallium acetate $CH_3(C_3H_5)TlOCOCH_3$. A chloroform solution (20 ml) of $(n\text{-}C_4H_9)_3SnC_3H_5$[9] (3 g) was added drop by drop to $CH_3Tl(CN)OCOCH_3$[14] (2.7 g) in methanol (400 ml) and the solution was stirred for 1 h at room temperature. After evaporating the solvents under reduced pressure, the remaining white residue was washed with diethyl ether (400 ml) to remove the ether soluble $(n\text{-}C_4H_9)_3SnCN$. The white solid was then recrystallized from chloroform/petroleum ether to give white needle-like crystals of this compound (1.8 g; 62%).

Methyl(allyl)thallium isobutyrate $CH_3(C_3H_5)TlOCO\text{-}i\text{-}C_3H_7$. Methyl(allyl)thallium isobutyrate was prepared by the reaction of $CH_3Tl(OCO\text{-}i\text{-}C_3H_7)_2$[15] (1.5 g) and $(n\text{-}C_4H_9)_3SnC_3H_5$ (1.6 g) in a manner similar to that described above to give white needle-like crystals of this compound (1.0 g; 63%).

Methyl(allyl)thallium *N,N*-dimethyldithiocarbamate or chloride, and tropolonate or propionate were prepared from the reaction of methyl(allyl)thallium acetate with $KSSCN(CH_3)_2$ or KCl in methanol, and with tropolone or propionic acid in chloroform/methanol, respectively. The properties of these compounds are summarized in Table 1.

TABLE 1

PROPERTIES OF METHYL(ALLYL)THALLIUM DERIVATIVES $CH_3(C_3H_5)TlY$

Y	M.p. (°C)	Analysis: found (calcd.) (%)		
		C	H	N
$OCOCH_3$	244–245 (decomp.)	22.29 (22.55)	3.50 (3.47)	
$OCOC_2H_5$	163–164	25.15 (25.12)	4.00 (3.93)	
$OCO\text{-}i\text{-}C_3H_7$	163–164	27.64 (27.65)	4.37 (4.35)	
$SSCN(CH_3)_2$	75–76	22.09 (22.09)	3.80 (3.71)	3.73 (3.68)
Tropolonate	224–225 (decomp.)	34.58 (34.62)	3.53 (3.43)	
Cl	>300	16.01 (16.23)	2.62 (2.72)	

Reactions of methyl(allyl)thallium compounds

With tetramethyltin. Methyl(allyl)thallium acetate (0.1 g; 0.3 mmole) and tetramethyltin (0.125 g; 0.7 mmole) were dissolved in dry methanol (0.465 g) and kept for 16 days at room temperature. The PMR spectrum showed that the peaks due to methyl(allyl)thallium acetate disappeared almost completely and were replaced by those attributed to dimethylthallium and trimethyltin moieties and an additional doublet of triplets at 8.23 ppm from tetramethyltin. The latter peaks disappeared after bubbling N_2 gas through the solution and were assigned to the methyl protons of propylene.

With palladous salts. $CH_3(C_3H_5)TlOCOC_2H_5$ (0.07 g; 0.2 mmole) and $Pd(OCOC_2H_5)_2$ (0.05 g; 0.2 mmole) were dissolved in $CDCl_3$ (0.48 g) at room temperature and the PMR spectrum was measured immediately. The peaks due to methyl(allyl)thallium propionate were not observed but new peaks attributed to monomethylthallium dipropionate [$J(Tl{-}CH_3) = 900$ Hz] and π-allylpalladium propionate (broad peaks due to π-allyl group at ca. 7.00, 6.00 and 4.40 ppm) appeared.

$CH_3(C_3H_5)TlOCOCH_3$ (0.16 g; 0.5 mmole) was reacted with $PdCl_2 \cdot 2C_6H_5CN$ (0.19 g; 0.5 mmole) in CH_2Cl_2 (40 ml) at room temperature. The white precipitate of $TlOCOCH_3$ was removed by filtration and the yellow filtrate* was evaporated under reduced pressure to give a yellow solid, which was recrystallized from CH_2Cl_2/petroleum ether to give $(\pi\text{-}C_3H_5PdCl)_2$ (0.08 g; 82 %), the melting point, IR and PMR spectrum of which were identical with those of an authentic sample[16]. A similar reaction of $CH_3(C_3H_5)TlOCOCH_3$ with $PdCl_2$ in CH_3OH/CH_2Cl_2 gave quantitatively $(\pi\text{-}C_3H_5PdCl)_2$ and $TlOCOCH_3$.

With rhodium(III) chloride. A reaction of $CH_3(C_3H_5)TlOCOCH_3$ (0.32 g; 1 mmole) with $RhCl_3 \cdot 3H_2O$ (0.14 g; 0.5 mmole) was carried out in CH_2Cl_2/absolute ethanol in a manner similar to that described for palladous chloride to give $[(\pi\text{-}C_3H_5)_2RhCl]_2$ (0.05 g), the PMR spectrum of which was identical with that of an authentic sample[17]. The red brown precipitates of TlCl and $RhCl_3$ were contaminated with $(CH_3)_2TlCl$, as was indicated by IR and PMR spectra.

TABLE 2

RELEVANT INFRARED VIBRATIONAL FREQUENCIES (IN CM^{-1}) OF SOME METHYL(ALLYL)THALLIUM COMPOUNDS $CH_3(C_3H_5)TlY$
In nujol mulls.

Y	$\nu(C{=}C)$	$\rho(Tl{-}CH_3)$	$\rho(Tl{-}CH_2)$	$\nu_{asym}(Tl{-}C)$	$\nu_{sym}(Tl{-}C)$ or $\delta(C{-}C{-}C)$
$OCOCH_3$[c]	1626 s	784 s	682 m	525 m	[a]
$OCOC_2H_5$	1626 s	782 s	680 m	524 m	474 w[b]
$OCO\text{-}i\text{-}C_3H_7$[c]	1626 s	781 s	680 m	[a]	476 w[b]
$SSCN(CH_3)_2$	1621 s	780 s	682 m	507 m	[a]
Tropolonate	1621 s	780 s	684 m	525 m	[a]
Cl	1626 s	788 s	673 m	528 m	470 m[b]

[a] Obscured by the absorption due to the ligand. [b] $\nu_{sym}(Tl{-}C)$ and $\delta(C{-}C{-}C)$ are overlapped. [c] The IR spectra of these compounds in $CHCl_3$ (5 wt. %) were almost identical with those in the solid state.

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* The PMR spectrum of the yellow filtrate showed a singlet peak at 6.99 ppm due to the decomposition product CH_3Cl of a possible intermediate, $CH_3Tl(Cl)OCOCH_3$. In addition, peaks attributed to $(\pi\text{-}C_3H_5PdCl)_2$, C_6H_5CN and CH_3COO protons were observed.

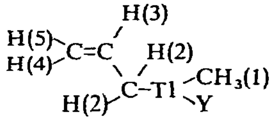
Reaction of RR'TlOCOCH$_3$ with Hg(OCOCH$_3$)$_2$

The PMR spectra of a methanol solution of RR'TlOCOCH$_3$ and Hg(OCOCH$_3$)$_2$ in a 1/1 mole ratio were measured after 6 min or 3 h at room temperature, and the peaks which appeared almost quantitatively were assigned to RTl(OCOCH$_3$)$_2$ and R'HgOCOCH$_3$ (R and R' = CH$_3$ and C$_6$H$_5$; CH$_3$ and C$_3$H$_5$; C$_2$H$_5$ and CH$_3$ or CH$_3$ and CN)*.

TABLE 3

J(Tl–H)[a] (IN Hz) AND τ[b] (IN PPM) FOR CH$_3$(C$_3$H$_5$)TlY

In CDCl$_3$ at 60 MHz and 20°.



Y	J(Tl–H)					Chemical shift τ				
	H(1)	H(2)[c]	H(3)[c]	H(4)[c,d]	H(5)[c,d]	H(1)	H(2)	H(3)	H(4)[d]	H(5)[d]
OCOCH$_3$	364	533	198	226	205	8.85	7.52	3.93	5.09	5.18
OCOC$_2$H$_5$	369	534	195	223	205	8.89	7.50	3.93	5.09	5.23
OCO-i-C$_3$H$_7$	365	532	197	222	198	8.87	7.51	3.96	5.12	5.22
SSCN(CH$_3$)$_2$	334	491	195	234	220	8.63	7.39	3.80	4.98	5.21
Tropolonate	359	[e]	[e]	[e]	[e]	8.89	[e]	[e]	[e]	[e]
Cl[f]	369	534	195	223	205	8.89	7.50	3.93	5.09	5.23

[a] The separation of $J(^{205}$Tl–H) and $J(^{203}$Tl–H) was not observed. [b] Relative to internal TMS (τ = 10.00 ppm). [c] J[H(2)–H(3)] = 8–9, J[H(3)–H(4)] = 15–16, J[H(3)–H(5)] = 9–10 Hz. J[H(2)–H(5)] and J[H(2)–H(4)] were not observed. [d] H(4) and H(5) were assigned by the difference of spin coupling constants with H(3). [e] Can not be detected in CDCl$_3$ and DMSO-d_6 because of the low solubility of this compound. [f] Measured in DMSO-d_6.

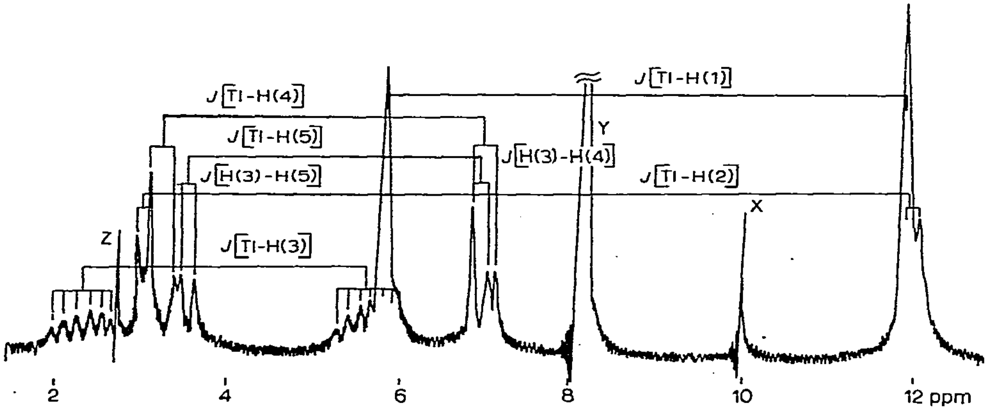


Fig. 1. PMR spectrum for CH$_3$(C$_3$H$_5$)TlOCOCH$_3$ in CDCl$_3$ at 60 MHz and 20°C. (X = TMS; Y = CH$_3$COO; Z = CHCl$_3$.)

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* Only CH$_3$Tl(OCOCH$_3$)$_2$ could be characterized.

Infrared spectra

The infrared spectra in nujol mulls and chloroform solution were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings. The results are shown in Table 2.

PMR spectra

The PMR spectra were measured on a Japan Electron Optics JNM-3H-spectrometer at 60 MHz and a Varian 3H-100 spectrometer operating at 100 MHz and 20°. The assignments of the methyl(allyl)thallium compounds were done by comparing the J(Tl–H) and the chemical shifts measured at 60 MHz with those at 100 MHz. J(Tl–H) and chemical shifts for the methyl(allyl)thallium derivatives and a typical spectrum are shown in Table 3 and Fig. 1, respectively.

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