

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 $\text{Hg}(\text{OCOCH}_3)_2$, PdX_2 ($\text{X} = \text{OCOC}_2\text{H}_5$ and Cl) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 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.

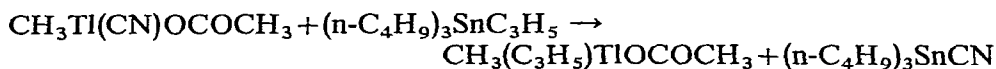
INTRODUCTION

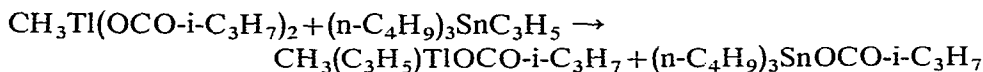
In the course of our studies^{1,2} on the reactions of mixed diorganothallium compounds, we have prepared a series of new methyl(allyl)thallium derivatives. Allylthallium compounds have not been reported previously, and it seemed of interest to determine whether the allyl-thallium bond is in dynamic 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 elements⁸.

In the novel replacement reaction¹ 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)tin⁹.



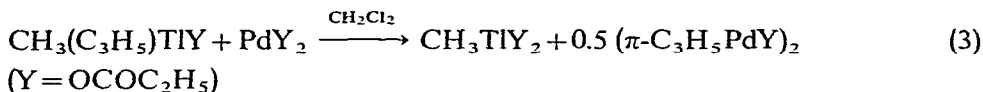
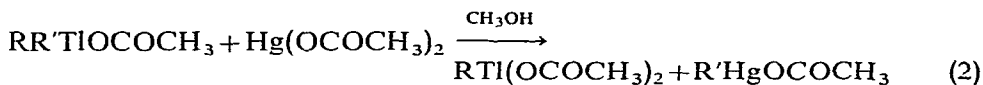
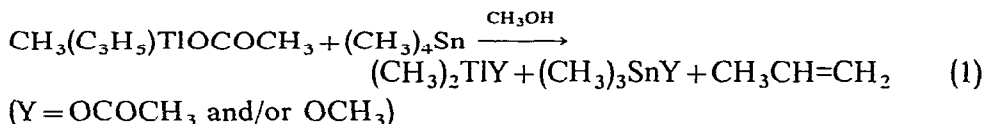


The carboxylates can be derivatized to $\text{CH}_3(\text{C}_3\text{H}_5)\text{TIY}$ using appropriate reagents, HY or KY ($\text{Y} = \text{Cl}$, $\text{SSCN}(\text{CH}_3)_2$, OCOC_2H_5 and tropolonate).

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, $\text{C}_3\text{H}_5\text{HgX}^7$ and $(\text{C}_3\text{H}_5)_n\text{SnR}_{4-n}^{10}$.

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 $J(\text{TI}-\text{CH}_3)$ and $J(\text{TI}-\text{CH}_2-)$ values and also a lower $\nu_{\text{asym}}(\text{TI}-\text{C})$ frequency. This may be suggestive of weaker TI-C bonds in the dithiocarbamate, as was reported to be the case in other diorganothallium dithiocarbamates². The fact that the $J(\text{TI}-\text{CH}_3)$ values for methyl(allyl)thallium derivatives, $\text{CH}_3(\text{C}_3\text{H}_5)\text{TIY}$, are smaller than those for the corresponding dimethylthallium compounds¹¹, $(\text{CH}_3)_2\text{TIY}$, 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 Bent¹² as in the case of organotin compounds¹³.

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 study¹ 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 $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_3\text{H}_5$, 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 $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$; $\text{R} = \text{CH}_3$, $\text{R}' = \text{CN}$ or $\text{R} = \text{C}_2\text{H}_5$, $\text{R}' = \text{CH}_3$.



The reaction with palladous propionate proceeds as shown in (3), but in the reactions with PdCl_2 and $\text{PdCl}_2 \cdot 2\text{C}_6\text{H}_5\text{CN}$, the monomethylthallium species decom-

posed to give CH_3Cl and TlOCOCH_3 . On the other hand, an unexpected product, $(\text{CH}_3)_2\text{TlCl}$, in addition to TlCl was obtained in the reaction with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.

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 $\text{R} = \text{CH}_3$ and $\text{R}' = \text{C}_3\text{H}_5$) or (3).

EXPERIMENTAL

Preparations

Methyl(allyl)thallium acetate $\text{CH}_3(\text{C}_3\text{H}_5)\text{TlOCOCH}_3$. A chloroform solution (20 ml) of $(\text{n-C}_4\text{H}_9)_3\text{SnC}_3\text{H}_5$ ⁹ (3 g) was added drop by drop to $\text{CH}_3\text{Tl}(\text{CN})\text{OCOCH}_3$ 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 $(\text{n-C}_4\text{H}_9)_3\text{SnCN}$. 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 $\text{CH}_3(\text{C}_3\text{H}_5)\text{TlOCO-i-C}_3\text{H}_7$. Methyl(allyl)-thallium isobutyrate was prepared by the reaction of $\text{CH}_3\text{Tl}(\text{OCO-i-C}_3\text{H}_7)_2$ ¹⁵ (1.5 g) and $(\text{n-C}_4\text{H}_9)_3\text{SnC}_3\text{H}_5$ (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 $\text{KSSCN}(\text{CH}_3)_2$ 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 $\text{CH}_3(\text{C}_3\text{H}_5)\text{TlY}$

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)	
$\text{OCO-i-C}_3\text{H}_7$	163–164	27.64 (27.65)	4.37 (4.35)	
$\text{SSCN}(\text{CH}_3)_2$	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. $CH_3(C_3H_5)TiOCOC_2H_5$ (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.

$CH_3(C_3H_5)TiOCOCH_3$ (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 $TiOCOCH_3$ 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 $(\pi-C_3H_5PdCl)_2$ (0.08 g; 82 %), the melting point, IR and PMR spectrum of which were identical with those of an authentic sample¹⁶. A similar reaction of $CH_3(C_3H_5)TiOCOCH_3$ with $PdCl_2$ in CH_3OH/CH_2Cl_2 gave quantitatively $(\pi-C_3H_5PdCl)_2$ and $TiOCOCH_3$.

With rhodium(III) chloride. A reaction of $CH_3(C_3H_5)TiOCOCH_3$ (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 $[(\pi-C_3H_5)_2RhCl]_2$ (0.05 g), the PMR spectrum of which was identical with that of an authentic sample¹⁷. The red brown precipitates of $TiCl$ and $RhCl_3$ were contaminated with $(CH_3)_2TiCl$, as was indicated by IR and PMR spectra.

TABLE 2

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

Y	$\nu(C=C)$	$\rho(Tl-CH_3)$	$\rho(Tl-CH_2)$	$\nu_{asym}(Ti-C)$	$\nu_{sym}(Ti-C)$ 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
$OCO-i-C_3H_7^c$	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 $\nu_{sym}(Ti-C)$ 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.

* 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, $CH_3Ti(Cl)OCOCH_3$. In addition, peaks attributed to $(\pi-C_3H_5PdCl)_2$, C_6H_5CN and CH_3COO protons were observed.

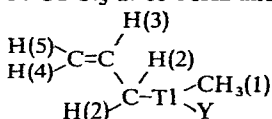
Reaction of $RR'TlOCOCH_3$ with $Hg(OCOCH_3)_2$

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 $RtI(OCOCH_3)_2$ and $R'HgOCOCH_3$ (R and $R' = CH_3$ and C_6H_5 ; CH_3 and C_3H_5 ; C_2H_5 and CH_3 or CH_3 and CN)^{*}.

TABLE 3

$J(Tl-H)^a$ (IN HZ) AND τ^b (IN PPM) FOR $CH_3(C_3H_5)TlY$

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
OCO_2H_5	369	534	195	223	205	8.89	7.50	3.93	5.09	5.23
$OCO-i-C_3H_7$	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 $J(^{203}Tl-H)$ and $J(^{205}Tl-H)$ was not observed. ^b Relative to internal TMS ($\tau = 10.00$ 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 $DMSO-d_6$.

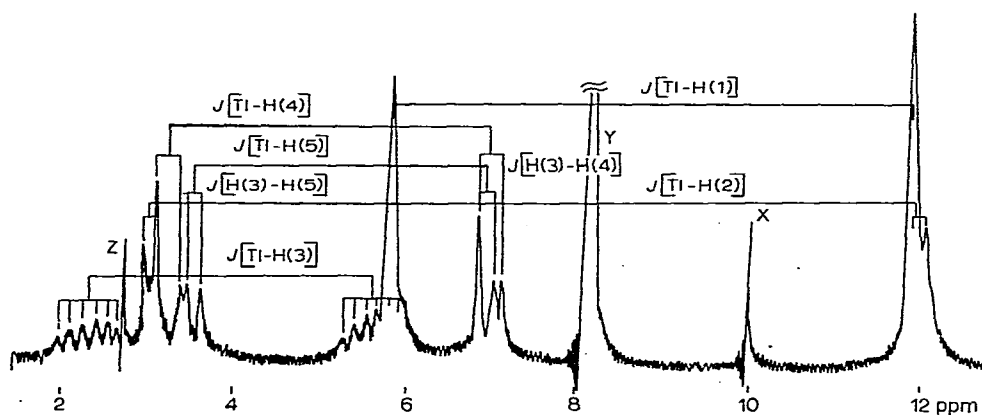


Fig. 1. PMR spectrum for $CH_3(C_3H_5)TlOCOCH_3$ in $CDCl_3$ at 60 MHz and 20°C. (X = TMS; Y = CH_3COO ; Z = $CHCl_3$.)

* Only $CH_3Tl(OCOCH_3)_2$ 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 $J(\text{TI-H})$ and the chemical shifts measured at 60 MHz with those at 100 MHz. $J(\text{TI-H})$ 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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REFERENCES

- 1 M. TANAKA, H. KUROSAWA AND R. OKAWARA, *J. Organometal. Chem.*, 18 (1969) 49.
- 2 M. TANAKA, H. KUROSAWA AND R. OKAWARA, *J. Organometal. Chem.*, 21 (1970) 41.
- 3 (a) J. E. NORDLANDER AND J. D. ROBERTS, *J. Amer. Chem. Soc.*, 81 (1959) 1769;
(b) H. E. ZIEGER AND J. D. ROBERTS, *J. Org. Chem.*, 34 (1969) 1976.
- 4 K. H. THIELE AND P. ZDUNNECK, *J. Organometal. Chem.*, 4 (1965) 10.
- 5 K. H. THIELE AND J. KÖHLER, *J. Organometal. Chem.*, 7 (1967) 365.
- 6 (a) V. S. BOGDANOV, Y. N. BUBNOV, S. I. FROLOV AND B. M. MIKHAILOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 307;
(b) Y. N. BUBNOV, S. I. FROLOV AND B. M. MIKHAILOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 824.
- 7 (a) W. KITCHING AND B. F. HEGARTY, *J. Organometal. Chem.*, 16 (1969) 39;
(b) A. N. NESMEYANOV, A. N. RUBEZHOV, L. A. LEITES AND S. P. GUBIN, *J. Organometal. Chem.*, 12 (1968) 187;
(c) H. E. ZIEGLER AND J. D. ROBERTS, *J. Org. Chem.*, 34 (1969) 2826.
- 8 M. L. H. GREEN AND P. L. I. NAGY, *Advan. Organometal. Chem.*, 2 (1964) 325.
- 9 W. J. JONES, W. C. DAVIES, S. T. BOWDER, C. E. EDWARDS, V. E. DAVIES AND L. H. THOMAS, *J. Chem. Soc.*, (1947) 1446.
- 10 K. KAWAKAMI AND H. G. KUIVILA, *J. Org. Chem.*, 34 (1969) 1502.
- 11 H. KUROSAWA AND R. OKAWARA, unpublished results.
- 12 H. A. BENT, *Chem. Rev.*, 61 (1961) 275.
- 13 J. R. HOLMES AND H. D. KAESZ, *J. Amer. Chem. Soc.*, 83 (1961) 3903.
- 14 T. FUKUMOTO, H. KUROSAWA AND R. OKAWARA, *J. Organometal. Chem.*, 22 (1970) 627.
- 15 H. KUROSAWA AND R. OKAWARA, *J. Organometal. Chem.*, 10 (1967) 211.
- 16 See ref. 8.
- 17 (a) K. C. RAMEY, D. C. LINI AND W. B. WISE, *J. Amer. Chem. Soc.*, 90 (1968) 4275;
(b) J. POWELL AND B. L. SHAW, *Chem. Commun.*, (1966) 302.

J. Organometal. Chem., 25 (1970) 353-358