

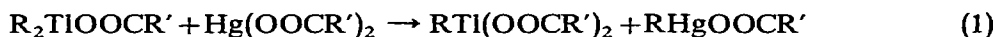
## PREPARATION AND PROPERTIES OF MONOALKYLTHALLIUM DERIVATIVES

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In contrast to well-known dialkylthallium compounds, monoalkylthallium derivatives have been thought to be very unstable and have never been isolated. Although in 1935 Melnikov and Gratscheva reported the preparation of several alkylthallium dihalides from dialkylthallium halides and thallic halides<sup>1</sup>, Sarrach<sup>2</sup> and Hart and Ingold<sup>3</sup> failed to confirm this work. However, we demonstrated in the previous paper<sup>4</sup> the existence of monomethylthallium species by the analysis of the PMR spectra of the reaction system (1) where  $R = R' = CH_3$ .



We now report a method for preparing several monomethyl- and monoethylthallium derivatives according to the reaction (1). Some interesting properties and the structural studies on the newly prepared monoalkylthallium compounds will also be described.

### EXPERIMENTAL

#### General comments

All the experiments except for decomposition runs were carried out at room temperature.

#### Starting materials

Dialkylthallium carboxylates were prepared from dialkylthallium carbonates<sup>5</sup> and the appropriate carboxylic acids in methanol, and mercuric carboxylates from mercuric oxide (yellow) and the appropriate carboxylic acids. These starting materials were found to be analytically pure.

#### Preparation of monoalkylthallium derivatives

*Methylthallium diacetate*<sup>6</sup>,  $CH_3Tl(OOCCH_3)_2$ . Dimethylthallium acetate (2.9 g; 10 mmole) and mercuric acetate (3.2 g; 10 mmole) were dissolved in 30 ml of dry methanol and the solution was allowed to stand for 4 h. To the residual solid obtained by vacuum evaporation was added 200 ml of benzene, and the soluble methylmercury acetate was separated by filtration. The remaining white solid was recrystallized from chloroform to give 1.4 g of  $CH_3Tl(OOCCH_3)_2$  (40%); m.p. 102–103° (dec.). (Found: C, 17.58; H, 2.58; Tl, 59.95.  $C_5H_9O_4Tl$  calcd.: C, 17.80; H, 2.69; Tl, 60.55%.)

*Methylthallium diisobutyrate*,  $CH_3Tl(OOCC_3H_7-iso)_2$ . Dimethylthallium isobutyrate (3.2 g; 10 mmole) and mercuric isobutyrate (3.7 g; 10 mmole) were dissolved

in 100 ml of chloroform. After 5 h the solution was concentrated by vacuum evaporation and the white needle-like crystals obtained were recrystallized from benzene/petroleum ether (2.4 g; 60%); m.p. 130–131° (dec). (Found: C, 27.36; H, 4.28; Tl, 51.55.  $C_9H_{17}O_4Tl$  calcd.: C, 27.46; H, 4.35; Tl, 51.92%.)

*Methylthallium dioxinate*,  $CH_3Tl(Ox)_2$ . To a methanol solution (20 ml) of 8-hydroxyquinoline (2.9 g; 20 mmole) was added slowly under stirring an aqueous solution (70 ml) of methylthallium diacetate (3.4 g; 10 mmole). The fine greenish yellow precipitate produced immediately was dried under vacuum (2.5 g; 50%); m.p. 160–161° (dec). (Found: C, 45.07; H, 3.24; N, 5.52; Tl, 40.12.  $C_{19}H_{15}N_2O_2Tl$  calcd.: C, 44.95; H, 2.98; N, 5.52; Tl, 40.25%.)

*Ethylthallium diisobutyrate*,  $C_2H_5Tl(OOCC_3H_7-iso)_2$  (M. Tanaka). This compound was prepared in a manner similar to that for methylthallium diisobutyrate. White, fluffy crystals were recrystallized from chloroform (60%); m.p. 121–122° (dec). (Found: C, 29.47; H, 4.51; Tl, 49.97.  $C_{10}H_{19}O_4Tl$  calcd.: C, 29.47; H, 4.70; Tl, 50.14%.)

*Ethylthallium dioxinate*,  $C_2H_5Tl(Ox)_2$  (M. Tanaka). This was prepared by a procedure essentially similar to that for methylthallium dioxinate (68%); m.p. 154–155° (dec). (Found: C, 46.15; H, 3.51; Tl, 38.75.  $C_{20}H_{17}N_2O_2Tl$  calcd.: C, 46.04; H, 3.28; Tl, 39.17%.)

#### Decomposition of methylthallium dicarboxylates

(i) An aqueous solution (20 ml) of methylthallium diacetate (0.5 g) was heated at 100° for 10 min and concentrated to give 0.39 g of thallos acetate (99%). Gas chromatography and the PMR spectra of the solution indicated the presence of methyl acetate (60%) and methanol (30%), together with acetic acid. A similar result was obtained with methylthallium diisobutyrate.

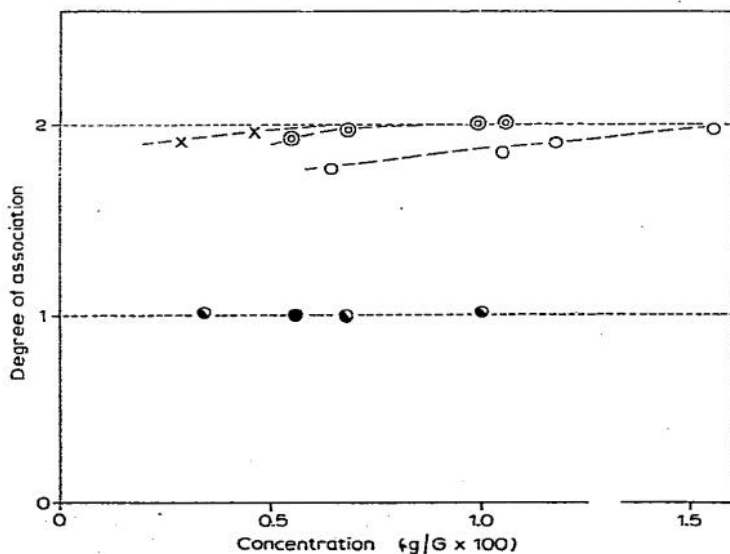


Fig. 1. Degree of association of alkylthallium derivatives in  $CHCl_3$  at 25°. ●  $CH_3Tl(Ox)_2$ ; ●  $C_2H_5Tl(Ox)_2$ ; ○  $CH_3Tl(OOCC_3H_7-iso)_2$ ; ×  $C_2H_5Tl(OOCC_3H_7-iso)_2$ ; ○  $(C_2H_5)_2TlOCC_3H_7-iso$ .

(ii) To an aqueous solution of methylthallium diacetate (0.5 g) was added 0.3 g of sodium chloride in the same solvent. Thallous chloride was precipitated immediately (almost quantitative) and gas chromatography of the gaseous product of the reaction indicated the presence of methyl chloride. Similarly, thallous bromide and methyl bromide or thallous iodide and methyl iodide were detected when the bromide or iodide anion was added to  $\text{CH}_3\text{Tl}(\text{OOCCH}_3)_2$ .

#### Molecular weight

Molecular weights of representative monomethyl- and monoethylthallium derivatives and diethylthallium isobutyrate were determined using a Mechrolab vapor pressure osmometer Model 302 in chloroform at 25°. Results are shown in Fig. 1.

#### Ultraviolet spectra

The ultraviolet spectra of methyl- and ethylthallium dioxinates were measured in dry benzene on a Hitachi EPS-2 spectrophotometer using 1 cm cells. The absorption spectra are shown in Fig. 2.

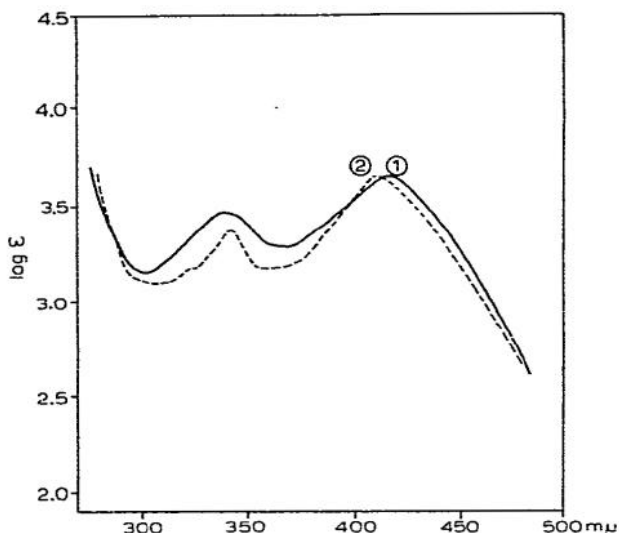


Fig. 2. Absorption spectra of  $\text{RTl}(\text{Ox})_2$  in benzene. 1.  $\text{R} = \text{C}_2\text{H}_5$ ;  $\lambda_{\text{max}} 415$ ,  $\epsilon_{\text{max}} 4.6 \times 10^3$ ; 2,  $\text{R} = \text{CH}_3$ :  $\lambda_{\text{max}} 410$ ,  $\epsilon_{\text{max}} 4.4 \times 10^3$ .

#### Infrared spectra

The infrared spectra were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings. Spectra were obtained in either Nujol or hexachlorobutadiene mulls and in chloroform solutions. The typical spectra for methylthallium diisobutyrate are shown in Fig. 3 together with that for diethylthallium isobutyrate in the 6–8  $\mu$  region, and the relevant infrared frequencies are given in Table 1.

#### PMR spectra

The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 Mc/s and 20°. A Varian 3H-100 spectrometer operating at 100 Mc/s

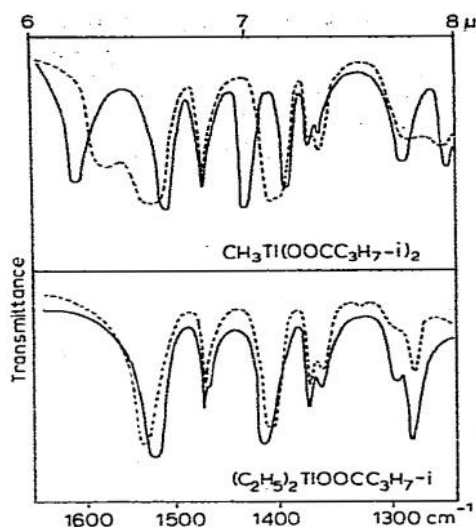


Fig. 3. Infrared spectra of alkylthallium isobutyrate. — solid; ---- solution (1 wt. % in  $\text{CHCl}_3$ ).

TABLE I

RELEVANT INFRARED VIBRATION FREQUENCIES OF SOME ALKYLTHALLIUM ISOBUTYRATES  
s, strong; m, medium; br, broad; sh, shoulder

$\text{CH}_3\text{Tl}(\text{OOCC}_3\text{H}_7\text{-iso})_2$		$\text{C}_2\text{H}_5\text{Tl}(\text{OOCC}_3\text{H}_7\text{-iso})_2$		$(\text{C}_2\text{H}_5)_2\text{TlOOCC}_3\text{H}_7\text{-iso}$		
Solid	Solution <sup>a</sup>	Solid	Solution <sup>a</sup>	Solid	Solution <sup>a</sup>	
1610 s	1577 br	1608 s	1580 br			} $\nu_{\text{asym.}}(\text{COO})$
1510 s	1525 s	1513 s	1527 s	1525 s	1542 s	
1425 s	1405 s	1422 s	1403 s	1410 s	1408 s	} $\nu_{\text{sym.}}(\text{COO})$
1390 s	1400 sh	1389 s	1399 sh			
1468 m	1469 s	1471 m	1468 m	1468 m	1470 m	} Additional bands around $\nu(\text{COO})$
1372 m	1370 m	1371 m	1370 m	1371 m	1368 m	
1359 m	1360 m	1359 m	1361 m	1360 m	1361 m	

<sup>a</sup> In chloroform (1–0.5 wt. %).

TABLE 2

$J(\text{Tl-H})$  (IN CPS) AND  $\tau$  (IN PPM) FOR SOME METHYLTHALLIUM DERIVATIVES  
Concentrations were 5 wt. %.

Compound	$J(^{205}\text{Tl-CH}_3)^a$			$\tau(\text{Tl-CH}_3)^b$	
	$\text{CHCl}_3$	$\text{CH}_3\text{OH}$	$\text{D}_2\text{O}$	$\text{CHCl}_3$	$\text{CH}_3\text{OH}$
$\text{CH}_3\text{Tl}(\text{OOCCH}_3)_2$	892	921	936	8.20	8.37
$\text{CH}_3\text{Tl}(\text{OOCC}_3\text{H}_7\text{-iso})_2$	902	923	931	8.17	8.35
$\text{CH}_3\text{Tl}(\text{Ox})_2$	790			8.34	
$(\text{CH}_3)_2\text{TlOOCC}_3\text{H}_7\text{-iso}$	377 <sup>c</sup>		405 <sup>c</sup>	8.96	

<sup>a</sup>  $J(^{203}\text{Tl-CH}_3)$  is 8–9 cps less than  $J(^{205}\text{Tl-CH}_3)$  except as noted. <sup>b</sup> Relative to internal TMS ( $\tau$  10.00 ppm).

<sup>c</sup>  $J(^{203}\text{Tl-CH}_3)$  is 3–4 cps less than  $J(^{205}\text{Tl-CH}_3)$ .

was used for methylthallium dioxinate because at 60 Mc/s the lower frequency signals of the doublets of methyl protons arising from  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  proton spin-spin coupling were obscured by the multiplet of oxinate ring protons. The PMR data of alkylthallium derivatives prepared in this work are given in Tables 2 and 3.

TABLE 3

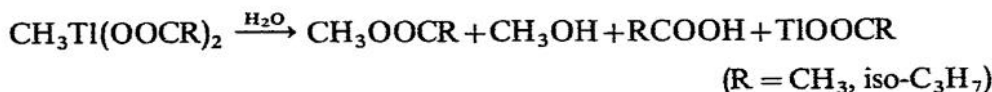
$J(\text{Tl-H})$  (IN CPS) AND  $\tau$  (IN PPM) FOR ETHYLTHALLIUM ISOBUTYRATES IN  $\text{CHCl}_3$  (0.5 WT. %).

Compound	$J(\text{Tl-CH}_2\text{-CH}_3)^a$	$J(\text{Tl-CH}_2)^a$	$\tau(\text{ethyl-CH}_3)^b$	$\tau(\text{ethyl-CH}_2)^b$
$\text{C}_2\text{H}_5\text{Tl}(\text{OOCCH}_2\text{CH}_2\text{-iso})_2$	1626	822	8.52	7.20
$(\text{C}_2\text{H}_5)_2\text{TlOOCCH}_2\text{CH}_2\text{-iso}$	612	306	8.45	8.16

<sup>a</sup> The separation of  $J(^{205}\text{Tl-H})$  and  $J(^{203}\text{Tl-H})$  was not obtained. <sup>b</sup> Relative to internal TMS ( $\tau$  10.00 ppm).

## DISCUSSION

Although methylthallium dicarboxylates are considerably stable in the solid state below the melting point, in an aqueous solution they decompose slowly at room temperature or rapidly when heated according to the following scheme:



The ease of reduction of these dicarboxylates may be compared with that of oxythallated intermediates in the oxidation of olefins<sup>7-9</sup> or cyclopropanes<sup>10</sup> by thallic acetate which decompose readily to give thallic acetate and the oxidation products of olefins or cyclopropanes. Halide anions react with  $\text{CH}_3\text{Tl}(\text{OOCR})_2$  to give thallic halides and methyl halides which were reported to be produced in attempts to prepare methylthallium dihalides<sup>1-3</sup>. If these facts are kept in mind, it seems noteworthy that monomethyl- and monoethylthallium compounds have been isolated for the first time only at room temperature as the dicarboxylate derivatives.

### *Penta-coordinated thallium atom in monoalkylthallium derivatives*

It has previously been known that the peak at 320  $m\mu$  of oxine shifts to longer wavelength, 370-430  $m\mu$  by chelation to metals<sup>11-13</sup>. In the ultraviolet spectra of methyl- and ethylthallium dioxinates in benzene (Fig. 2), the absorption peak is found at 410 and 415  $m\mu$  respectively. In addition, these compounds are monomeric in chloroform as shown in Fig. 1. Therefore, we believe that these oxinates are chelated in solution with the penta-coordinated thallium atom, similar to the reported phenylthallium dioxinate<sup>14</sup>.

The infrared spectra of methyl- and ethylthallium diisobutyrate both in the solid state and in solution show the four characteristic absorption bands assignable to  $-\text{OCO}-$  stretching vibrations as shown in Fig. 3 and Table 1. Among these, the bands at near 1525  $\text{cm}^{-1}$  and 1405  $\text{cm}^{-1}$  in the solution spectra may be associated with the bridging  $-\text{OCO}-$  group, because these diisobutyrate are dimeric in chloroform as shown in Fig. 4 and because the solution spectra of dimeric diethylthallium isobutyrate as written (I) (see Fig. 4) show the bands due to the bridging  $-\text{OCO}-$  unit

at  $1542\text{ cm}^{-1}$  and  $1408\text{ cm}^{-1}$  (Fig. 3 and Table 1). Now the remaining pair of bands at near  $1580\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  in solution suggests the existence of a non-ester type of isobutyryloxy group and may be due to the chelating one. Accordingly, we ten-

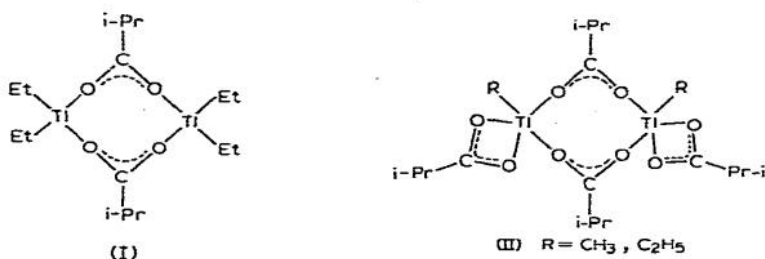


Fig. 4.

tatively suggest the structure of these diisobutyrylates in solution to be as shown (II), in which the thallium atom may also be penta-coordinated. In the solid state, however, other possibilities of the coordination around the thallium atom cannot necessarily be excluded.

#### PMR spectra of monoalkylthallium compounds

The PMR spectra of newly prepared monomethyl- and monoethylthallium derivatives show much larger  $J(\text{Tl-H})$  values than those for dimethyl- and diethylthallium compounds (Tables 2 and 3). We find that the ratios of  $J(\text{Tl-H})$  for methyl- or ethylthallium dicarboxylates to  $J(\text{Tl-H})^{15-17}$  for dimethyl- or diethylthallium derivatives are about  $2.3 \pm 0.3$ . These values are almost similar to  $J(\text{RTIY}_2)/J(\text{R}_2\text{TIY})$  observed for the aromatic and vinyl series<sup>15</sup>. The uniform increase in the  $J$  values in the series  $\text{R}_3\text{Tl}$ ,  $\text{R}_2\text{TIY}$  and  $\text{RTIY}_2$  irrespective of  $\text{R}$  was qualitatively interpreted as due to the increase in both the  $s$ -character in the  $\text{Tl-C}$  bond and in the effective nuclear charge of the thallium atom<sup>15,16</sup>. The smaller value of  $J(\text{Tl-CH}_3)$  for  $\text{CH}_3\text{Tl}(\text{Ox})_2$  than those for the other monomethylthallium derivatives could be understood in terms of the reduced  $s$ -character in the  $\text{Tl-C}$  bond of this compound as a result of somewhat stronger thallium-ligand covalent bond\*. The reason of the variation of the coupling constants in several solvents is not clear. One of the possible explanations is that the structural change of methylthallium dicarboxylates in an aqueous solution\*\* or methanol would bring about differences in the  $s$ -character in the  $\text{Tl-C}$  bond.

#### ACKNOWLEDGEMENTS

The authors wish to thank Dr. M. YOKOO of Takeda Chemical Instituté for assistance and suggestive discussions to this work.

\* Similar results were reported in the PMR spectra of several methyltin oxinates<sup>18,19</sup>.

\*\* The results of electric conductivity measurements in  $\text{H}_2\text{O}$  ( $A_{\text{mol}}$  81.4, 67.6 and  $54.0\text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  at concentrations  $2.14, 9.35$  and  $23.0 \times 10^{-3}\text{ mol/l}$  for  $\text{CH}_3\text{Tl}(\text{OOCCH}_3)_2$ ;  $A_{\text{mol}}$  72.7, 55.2 and  $41.6\text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  at concentrations  $1.71, 6.55$  and  $14.3 \times 10^{-3}\text{ mol/l}$  for  $\text{CH}_3\text{Tl}(\text{OOC}_3\text{H}_7\text{-iso})_2$ ) suggest the ionic dissociation of these compounds in an aqueous solution.

## SUMMARY

Several monomethyl- and monoethylthallium derivatives have been synthesized for the first time. Methylthallium dicarboxylates are found to decompose when heated or treated with halide anions to give thallos ion and methyl esters of carboxylic acids, methanol or methyl halides. From the structural studies on  $\text{RTl}(\text{Ox})_2$  and  $\text{RTl}(\text{OCC}_3\text{H}_7\text{-iso})_2$  ( $\text{R} = \text{CH}_3$  and  $\text{C}_2\text{H}_5$ ) in solution, it is suggested that these compounds have penta-coordinated thallium atoms.

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