Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REDISTRIBUTION REACTION OF SOME DIALKYLTHALLIUM(III) COMPOUNDS

MINORU TANAKA, HIDEO KUROSAWA AND ROKURO OKAWARA
Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka (Japan)

(Received June 17th, 1969)

SUMMARY

Some new methylethylthallium derivatives, as well as several dimethylthallium and diethylthallium compounds, were prepared. The compounds, $CH_3(C_2H_5)TlX$ where $X=SCH_3$, SC_6H_5, oxinate and tropolonate were found to redistribute into $(CH_3)_2TlX$ and $(C_2H_5)_2TlX$ at room temperature and/or at higher temperatures. The reverse reaction between $(CH_3)_2TlX$ and $(C_2H_5)_2TlX$ where $X=SCH_3$, SC_6H_5, oxinate, tropolonate and salicylaldehydate also took place with considerable ease, yielding the corresponding methylethylthallium derivative.

In contrast to mixed diorganomercury compounds[1,2], various mixed diorganothallium chlorides[3] and isobutyrates[4], which have been prepared recently in our laboratory, seem to be stable to redistribution up to about 100°. We report here the preparation of some new methylethylthallium derivatives which are tend to redistribute (eqn. 1).

$$2\,CH_3(C_2H_5)TlX \rightarrow (CH_3)_2TlX + (C_2H_5)_2TlX \qquad (1)$$

$X = SCH_3$, SC_6H_5, oxinate and tropolonate

The reaction between some dimethylthallium and diethylthallium compounds has also been found to proceed with considerable ease, yielding methylethylthallium derivatives (the reverse reaction).

EXPERIMENTAL

Dimethylthallium and diethylthallium derivatives

Dimethylthallium tropolonate or isobutyrate was prepared from dimethylthallium carbonate and tropolone or isobutyric acid in aqueous methanol. Dimethylthallium *N,N*-dimethyldithiocarbamate was prepared by the reported method[5]. The preparations of the other dimethylthallium compounds used in this study have been described[6].

The diethylthallium compounds were prepared by methods similar to those used to obtain the corresponding dimethylthallium compounds. The properties and analytical data of all new compounds are given in Table 1.

TABLE 1

PROPERTIES OF DIMETHYLTHALLIUM AND DIETHYLTHALLIUM DERIVATIVES

Compound	M.p. (°C)	Analysis, found (calcd.) (%)		
		C	H	N
$(CH_3)_2TlOCOC_3H_7$-iso	265–268 (dec.)	22.35 (22.41)	4.30 (4.08)	
$(CH_3)_2Tl(T)$[a]	273–275 (dec.)	29.87 (30.40)	3.25 (3.12)	
$(C_2H_5)_2TlOCOC_3H_7$-iso	218–219 (dec.)	27.04 (27.49)	5.12 (4.90)	
$(C_2H_5)_2TlSC_6H_5$	102–104	32.33 (32.32)	4.14 (4.07)	
$(C_2H_5)_2TlSCH_3$	48–49	19.40 (19.40)	4.38 (4.23)	
$(C_2H_5)_2Tl(Dtc)$[b]	118–119	21.98 (21.97)	4.27 (4.21)	3.63 (3.66)
$(C_2H_5)_2Tl(Ox)$[c]	215	38.26 (38.40)	4.05 (3.97)	3.44 (3.44)
$(C_2H_5)_2Tl(T)$[a]	211–212 (dec.)	34.36 (34.44)	4.11 (3.94)	
$(C_2H_5)_2Tl(Sal)$[d]	117–118[e]	34.09 (34.44)	4.31 (3.94)	

[a] T = tropolonate. [b] Dtc = *N,N*-dimethyldithiocarbamate. [c] Ox = oxinate = 8-hydroxyquinolinate. [d] Sal = salicylaldehydate. [e] Lit.[11] m.p. 116–118°.

Preparation of methylethylthallium derivatives

Unless otherwise specified, all the preparations were carried out at room temperature in order to avoid redistribution reactions. Some examples of the preparations of the new methylethylthallium derivatives listed in Table 2 are described below.

Methylethylthallium methanethiolate. To an aqueous solution (30 ml) of methylethylthallium isobutyrate[4] (1 g, 3 mmole) was added a slight excess of an aqueous solution of sodium methanethiolate. The white precipitate was washed with water and ether repeatedly. Yield 0.6 g, 68%. Methylethylthallium thiophenoxide (80%) and *N,N*-dimethyldithiocarbamate (62%) were prepared in a similar manner.

Methylethylthallium oxinate. To a pyridine solution (20 ml) of methylethylthallium chloride[3] (1.1 g, 3.2 mmole) was added a methanol solution (10 ml) of thallous oxinate (1 g, 3 mmole). After a day the white precipitate of thallous chloride was removed by filtration. Addition of water (60 ml) to the concentrated filtrate (about 8 ml) gave yellow crystals which were recrystallized from methanol (20 ml)/water (50 ml) to give 0.8 g of this compound (63%).

Methylethylthallium tropolonate. To an aqueous solution (30 ml) of methylethylthallium isobutyrate (1 g, 3 mmole) was added an aqueous solution (10 ml) of tropolone (0.4 g, 3.3 mmole), and the mixture was boiled under reflux for 2 h. The yellow crystals obtained were recrystallized from methanol (40 ml)/water (80 ml) to give 0.65 g of this compound (58%).

TABLE 2

PROPERTIES OF METHYLETHYLTHALLIUM DERIVATIVES, $CH_3(C_2H_5)TlX$

Compound X	M.p. (°C)	Analysis, found (calcd.) (%)				
		C	H	Tl	Mol.wt.[a]	Concn.[b]
SCH_3	81–83			68.70 (69.15)		
SC_6H_5	111–113	30.87 (30.23)	3.63 (3.66)	56.86 (57.14)		
Dtc[c,d]	128–129	19.50 (19.55)	4.22 (3.83)	55.38 (55.43)	395 (369)	1.08
Ox[c]	200 (dec.)	37.06 (36.71)	3.75 (3.59)	51.54 (52.03)	579 562 (393)	0.575 0.461
T[c]	240 (dec.)			54.96 (55.30)	493 521 534 (310)	0.593 0.849 0.930

[a] Measured in chloroform solution at 25° using a Mechrolab vapor pressure osmometer Model 302. [b] Concentration in wt.%. [c] Notations are the same as in Table 1. [d] Anal. N found 3.78, calcd. 3.80%.

Redistribution reactions

A benzene or toluene solution of each methylethylthallium derivative was refluxed for 5–10 h. After cooling to room temperature, occurrence of the redistribution reaction could be confirmed by means of IR and PMR spectra; $\nu_{asym}(TlC_2)$ frequencies in the reactants are *ca.* 20 cm^{-1} lower than those in the corresponding dimethylthallium compounds[6,7], and $J(Tl{-}CH_3)$ values in the former are *ca.* 40–60 Hz smaller than those in the latter[6,7].

The reverse reaction between dimethylthallium and diethylthallium compounds was carried out in refluxing toluene for 5 h. After evaporating the solvent at room temperature under vacuum, the residual mixture was dissolved in pyridine

TABLE 3

RESULTS OF THE REDISTRIBUTION REACTION,

$$(CH_3)_2TlX + (C_2H_5)_2TlX \rightarrow 2\ CH_3(C_2H_5)TlX$$

IN REFLUXING TOLUENE FOR 5 H

X	Initial concn. of $(CH_3)_2TlX$ (mol/l)[a]	Conversion (%)
SCH_3	0.053	53
SC_6H_5	0.038	48
Dtc[b]	0.026	0
Ox[b]	0.025	47
Sal[b]	0.030	28
T[b]	0.018	17
$OCOC_3H_7$-iso	0.022	Trace

[a] Equimolar amounts of the dimethylthallium and diethylthallium compounds were used. [b] Notations are the same as in Table 1.

(concn. 10–20 wt.%). PMR spectra were immediately recorded to determine the degree of conversion on the basis of the peak area ratio of methyl signals of dimethylthallium and methylethylthallium derivatives. Results are shown in Table 3.

Infrared spectra

The infrared spectra were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings. The assignments of Tl–C stretching and $CH_3(Tl)$ and $CH_2(Tl)$ rocking vibrations in methylethylthallium derivatives were carried out by comparison to the spectra of corresponding dimethylthallium and diethylthallium compounds. The frequencies of these modes are given in Table 4.

TABLE 4

RELEVANT INFRARED ABSORPTION FREQUENCIES (cm^{-1})[a] AND SPIN–SPIN COUPLING CONSTANTS (Hz)[b] OF METHYLETHYLTHALLIUM DERIVATIVES, $CH_3(C_2H_5)TlX$

Compound X	Rocking		TlC_2 stretching		$J(Tl\text{–}CH_3)$[c]
	$CH_3(Tl)$	$CH_2(Tl)$	ν_{asym}	ν_{sym}	
SCH_3	741 (s)	673 (s) 668 (s)	501 (s)	448 (m)	304[f]
SC_6H_5	762 (s)	676 (s)	508 (s)	444 (m)	294
Dtc[d]	759 (s)	676 (s)	511 (s)	[e]	301[f]
Ox[d]	759 (s)	678 (s)	518 (s)	458 (w)	345
$OCOC_3H_7$-iso	769 (s)	680 (m)	[e]	468 (w)	331
T[d]	771 (s)	681 (m)	535 (s) 528 (s)	472 (m)	338
Sal[d]					334[g]

[a] Measured in Nujol mulls and/or in chloroform solution (2–3 wt.%). [b] In $CDCl_3$ solution (8–15 wt.%). [c] Separation of $J(^{205}Tl\text{–}CH_3)$ and $J(^{203}Tl\text{–}CH_3)$ was not observed except when noted. [d] Notations are the same as in Table 1. [e] Obscured by the absorptions due to the ligand. [f] The values of $J(^{205}Tl\text{–}CH_3)$. $J(^{203}Tl\text{–}CH_3)$ is smaller than $J(^{205}Tl\text{–}CH_3)$ by 3–4 Hz. [g] Obtained from a redistributed mixture of dimethylthallium and diethylthallium salicylaldehydates.

PMR spectra

The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 MHz and 20°, and a Varian 3H-100 spectrometer operating at 100 MHz and 20°. $J(Tl\text{–}CH_3)$ values in methylethylthallium compounds are shown in Table 4.

DISCUSSION

Of the several mixed diorganothallium compounds studied, only methylethylthallium methanethiolate and thiophenoxide redistribute easily even at room temperature. This was observed during the course of PMR measurements of these compounds in chloroform or benzene solution. On the other hand, methylethylthallium oxinate, isobutyrate and tropolonate in which the ligands are bonded to thallium through oxygen and/or nitrogen do not change after 10 h in refluxing benzene. However, these compounds were found to redistribute gradually in refluxing toluene*, and the reverse reaction also occurs at this temperature as shown in Table 3**.

The extreme ease of the redistribution reactions of methylethylthallium methanethiolate and thiophenoxide and their reverse reactions can be understood in terms of the weaker Tl–C bonds in these compounds. The weaker Tl–C bonds in methylethylthallium methanethiolate and thiophenoxide may be deduced, as in the case of dimethylthallium compounds[6,7], from smaller Tl–C stretching, $CH_3(Tl)$ and $CH_2(Tl)$ rocking frequencies and smaller $Tl–CH_3$ spin–spin coupling constants in these compounds, as shown in Table 4.

Although methylethylthallium dithiocarbamate may also have weaker Tl–C bonds judging from the parameters in Table 4, it is very stable to redistribution. The reason for this is not clear at this stage. However, it may have some connection with the fact that this compound is monomeric (Table 2), probably as a result of strong coordination of a bidentate dithiocarbamate ligand [ν(C=N) at 1490 cm^{-1} and appearance of only one intense band at 975 cm^{-1} in the region 1000 ± 70 cm^{-1}, *cf.* ref. 5]. On the other hand, the other dialkylthallium compounds capable of redistributing are more or less associated in solution, the degree of association being between 1 and 2 [$(CH_3)_2TlSR$[6,9], $(C_2H_5)_2TlOCOC_3H_7$-iso[10], $(C_2H_5)_2Tl(Sal)$[11], and $CH_3(C_2H_5)Tl(Ox)$ and $CH_3(C_2H_5)Tl(T)$ (Table 2)], although the latter four compounds have a bidentate ligand and hence may contain a thallium atom with a coordination number higher than four.

ACKNOWLEDGEMENT

We thank Prof. D. G. White of The George Washington University for his help in improving our manuscript.

REFERENCES

1 M. S. Kharasch and R. Marker, *J. Amer. Chem. Soc.*, 48 (1926) 3130.
2 G. F. Reynolds and S. R. Daniel, *Inorg. Chem.*, 6 (1967) 480; and references therein.
3 M. Tanaka, H. Kurosawa and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 1565.
4 M. Tanaka, H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 18 (1969) 49.
5 F. Bonati, S. Cenini and R. Ugo, *J. Organometal. Chem.*, 9 (1967) 395.
6 H. Kurosawa, K. Yasuda and R. Okawara, *Bull. Chem. Soc. Jap.*, 40 (1967) 861.
7 H. Kurosawa and R. Okawara, *Trans. N.Y. Acad. Sci., Ser. II*, 30 (1968) 962; and unpublished results.
8 J. V. Hatton, *J. Chem. Phys.*, 40 (1964) 933.
9 G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, (1956) 3351.
10 H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 10 (1967) 211.
11 G. H. W. Milburn and M. R. Truter, *J. Chem. Soc., A*, (1967) 648.

---

* Preliminary results indicate that it takes more than 5 h of refluxing for the redistribution to proceed to equilibrium.

** Relevant to these results is the report[8] that the PMR spectrum of a mixture of dimethylthallium and diethylthallium nitrates or lactates in D_2O at 27° can be interpreted only as the superposition of the individual spectra.