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NOTE

SOME METHYL(PHENYLETHYNYL)- AND METHYL(CYANO)-THALLIUM DERIVATIVES

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Diorganothallium salts have long been known to be among the most stable organometallic compounds. Some monomethyl- and monoethylthallium compounds which were recently prepared in this laboratory[1] and monophenylthallium dichloride have been shown to react readily with arylboronic acids or tetraalkyltins, giving mixed diorganothallium compounds such as $(CH_3)(C_6H_5)TlCl$[2], $(C_2H_5)(C_6H_5)TlCl$[2], $(CH_3)(C_2H_5)TlCl$[2] and $(C_6H_5)(p\text{-}CH_3C_6H_4)TlCl$[3].

We report here some new routes for the preparation of other mixed diorganothallium compounds containing phenylethynyl or cyano substituents from monomethylthallium derivatives.

Methylthallium diacetate[1] was hydrolyzed by aqueous KOH to give amorphous, white, powdery CH_3TlO. This reacted with phenylacetylene in refluxing methanol in air, forming an amorphous organothallium derivative, probably methyl (phenylethynyl)thallium carbonate as indicated by its IR spectrum. When this product was treated with an equimolar quantity of acetic acid, the expected mixed diorganothallium acetate, $(CH_3)(C_6H_5C{\equiv}C)TlOOCCH_3$, was obtained. This product was further converted by $NaB(C_6H_5)_4$ into $[(CH_3)(C_6H_5C{\equiv}C)Tl]B(C_6H_5)_4$.

$CH_3Tl(CN)(OOCCH_3)$ was precipitated when a chloroform solution of $CH_3Tl(OOCCH_3)_2$ was added to an excess of $(CH_3)_3SnCN$ in the same solvent. An attempt to isolate $[CH_3TlCN]B(C_6H_5)_4$ from $CH_3Tl(CN)(OOCCH_3)$ and $NaB(C_6H_5)_4$ was unsuccessful due to the production of $[(CH_3)(C_6H_5)Tl]B(C_6H_5)_4$ which also can be prepared from $(CH_3)(C_6H_5)TlCl$ and $NaB(C_6H_5)_4$. In this connection, some preliminary results indicate that the reaction between monoalkylthallium compounds such as $RTl(OOCC_3H_7\text{-iso})_2$ ($R = CH_3$, C_2H_5 and C_6H_5) and $NaB(C_6H_5)_4$ is a convenient method for the preparation of $[R(C_6H_5)Tl]B(C_6H_5)_4$, and details of this reaction will be reported later.

In the IR and Raman spectra of methyl(phenylethynyl)- and methyl(cyano)-thallium compounds, the position of $\nu(C{\equiv}C)$ or $\nu(C{\equiv}N)$ (Table 1) is indicative of the existence of covalently bonded $C{\equiv}C$[4] or $C{\equiv}N$[5] groups. Thus, as expected from the formation of C–Tl–C moiety in these compounds, $(CH_3)(C_6H_5C{\equiv}C)TlX$ ($X = OOCCH_3$ and $B(C_6H_5)_4$) are not hydrolyzed by water, which may be compared with the water sensitive $(CH_3)_2Tl(C{\equiv}CC_6H_5)$[4] and $Na[(C_6H_5C{\equiv}C)_4Tl]$[4]; also, unlike thermally unstable $CH_3Tl(OOCCH_3)_2$[1], $CH_3Tl(CN)(OOCCH_3)$ is stable to such a degree that it can be recovered unchanged from hot aqueous methanolic solution.

TABLE 1

PROPERTIES OF SOME METHYLTHALLIUM COMPOUNDS

Compound	M.p. (°C)	Analysis found (calcd.) (%) C	H	Tl	$\nu(C\equiv C)$ or $\nu(C\equiv N)^a$ (cm^{-1})
$(CH_3)(C_6H_5C\equiv C)TlOOCCH_3$	145–147	34.50 (34.81)	3.17 (2.92)	53.66 (53.84)	2151
$[(CH_3)(C_6H_5C\equiv C)Tl]B(C_6H_5)_4$	>250	61.80 (61.96)	4.54 (4.41)		2160
$CH_3Tl(CN)(OOCCH_3)$	159–160	15.91 (15.78)	2.18 (1.99)	66.74 (67.12)	2193 2194^b
CH_3TlO	200 (decompn.)	5.66 (5.10)	1.27 (1.28)	86.48 (86.82)	
$[(CH_3)(C_6H_5)Tl]B(C_6H_5)_4$	>250	59.87 (60.47)	4.72 (4.58)		

[a] IR in Nujol mulls except as noted. [b] Raman in H_2O (4 wt. %).

TABLE 2

$J(Tl\text{-}CH_3)$ (IN CPS) AND $\delta(CH_3\text{-}Tl)$ (IN PPM)[a] FOR SOME $(CH_3)(R)TlOOCCH_3$ IN D_2O[b]

R	$J(^{205}Tl\text{-}CH_3)^c$	$\delta(CH_3\text{-}Tl)$
C_2H_5	354	+2.68
CH_3	405	+2.57
C_6H_5	455	+2.38
$C_6H_5C\equiv C$	672	+2.26
CN	828	+2.15

[a] Relative to internal dioxane. [b] Concentrations were 0.5–2.5 wt. %. [c] $J(^{203}Tl\text{-}CH_3)$ was 3–4 cps less for $R = C_2H_5$, CH_3 and C_6H_5 and 5–7 cps less for $R = C_6H_5C\equiv C$ and CN than $J(^{205}Tl\text{-}CH_3)$.

In Table 2 are given $J(Tl\text{-}CH_3)$ values and chemical shifts of methyl protons attached to thallium for some methylthallium acetates measured in D_2O. From the Table it is clear that in these compounds, which are assumed to have a similar C–Tl–C configuration in water*, J values increase and chemical shifts move downfield with increasing electron-attracting power of the group R. This variation of J values is consistent with the proposal that Fermi contact interaction is the dominant coupling mechanism in Tl–H spin coupling[6,7]. A similar result was reported in the PMR spectra of alkylmercury compounds[8].

EXPERIMENTAL

Methylthallium oxide

To an aqueous solution (50 ml) of methylthallium diacetate[1] (3.4 g) was added

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* The results of electric conductivity measurements of $(CH_3)(C_6H_5C\equiv C)TlOOCCH_3$ and $CH_3Tl(CN)(OOCCH_3)$ suggest ionic dissociation of these compounds in an aqueous solution similar to that observed with the well known dimethylthallium salts.

dropwise aqueous KOH solution until no further precipitate of CH_3TlO was obtained. The white powder obtained was dried under vacuum. The yield was 1.75 g (75%). The product is insoluble in water and common organic solvents.

Methyl(phenylethynyl)thallium acetate

CH_3TlO (2.35 g) and phenylacetylene (1.5 g) were heated in 100 ml of methanol on a water bath until all of the oxide had disappeared. Evaporation of the solvent at 40–50° gave white solid, the IR spectrum of which showed $\nu(C{\equiv}C)$ at 2155 cm^{-1}, $\rho(CH_3)$ at 806 cm^{-1}, $\nu(Tl{-}CH_3)$ at 530 cm^{-1} and very broad, strong bands at 1475 and 1320 cm^{-1} characteristic of carbonate ion. This product, presumably methyl(phenylethynyl)thallium carbonate was dissolved in 50 ml of methanol containing 0.6 g of acetic acid, and $(CH_3)(C_6H_5C{\equiv}C)TlOOCCH_3$ crystallized on standing for a day. Yield 2.6 g (70%). Λ_{mol} in H_2O at 25°, 62 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ at a concentration of 4.70×10^{-3} *M*.

Methyl(phenylethynyl)thallium tetraphenylborate

To an aqueous methanolic solution (50 ml) of 1.9 g of $(CH_3)(C_6H_5C{\equiv}C)TlOOCCH_3$ was added 1.7 g of $NaB(C_6H_5)_4$ in H_2O. The white solid obtained after evaporation of methanol was dried under vacuum (2.2 g; 70%).

Methyl(cyano)thallium acetate

A chloroform solution (70 ml) of $CH_3Tl(OOCCH_3)_2$ (3.4 g) was added to $(CH_3)_3SnCN$ (2 g) in the same solvent (30 ml). The white precipitate immediately obtained was recrystallized from methanol. Yield 2.1 g (70%). Λ_{mol} in H_2O at 25°, 74 and 84 $ohm^{-1}\cdot cm^2\cdot mol^{-1}$ at concentrations of 1.09×10^{-2} and 3.29×10^{-3} *M*, respectively.

Methylphenylthallium tetraphenylborate

To an aqueous solution of $CH_3Tl(CN)(OOCCH_3)$ (1.5 g) was added drop by drop aqueous $NaB(C_6H_5)_4$ solution until no more precipitate was obtained. The white, amorphous solid was recrystallized from acetone to give 2.4 g of $[(CH_3)(C_6H_5)Tl]B(C_6H_5)_4$ (80%). The same product was obtained from $(CH_3)(C_6H_5)TlCl$[2] and $NaB(C_6H_5)_4$ and also from $CH_3Tl(OOCC_3H_7\text{-iso})_2$[1] and $NaB(C_6H_5)_4$.

The properties and analytical data of the methylthallium compounds prepared in this work are summarized in Table 1.

Methylethylthallium- or methylphenylthallium acetate was prepared from $(CH_3)(C_2H_5)TlCl$[2] or $(CH_3)(C_6H_5)TlCl$[2] and $AgOOCCH_3$ in methanol, and used for the PMR measurements without analysis.

The infrared spectra were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings in Nujol and hexachlorobutadiene mulls. A Raman spectrum of $CH_3Tl(CN)(OOCCH_3)$ was obtained using a Nippon–Yuki–Gosei spectrograph. The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer at 60 Mc/s and 20°.

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