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PREPARATION OF MONOMETHYL- AND MONOETHYLTHALLIUM COMPOUNDS BY MEANS OF SOME METHYL- AND ETHYLTIN DERIVATIVES

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SUMMARY

Methyl- or ethyl(cyano)thallium acetate has been prepared by using a methyltin or ethyltin compound, such as $(CH_3)_2SnF_2$, $(CH_3)_3SnOAc$, $(CH_3)_4Sn$ or $(C_2H_5)_4Sn$, together with thallic acetate and sodium cyanide.

The reactions of some methyltin derivatives with thallic acetate in the absence of cyanide anion have also been investigated.

INTRODUCTION

Some monoalkylthallium dicarboxylates (alkyl = methyl, ethyl and n-propyl) have been synthesized from dialkylthallium carboxylates and mercuric carboxylates[1,2]. We also have reported the preparation of methyl(cyano)thallium acetate by the reaction of ammonium methylpentafluorosilicate with thallic acetate in the presence of sodium cyanide[3]. On the other hand, monoethylthallium compounds could not be obtained from the reactions of some ethyltin or ethyllead derivatives with thallic chloride[4-6], although Borisov and Novikova reported the preparation of some monoaryl- and monovinylthallium dichlorides by an analogous reaction of some organotin compounds with thallic chloride[6]. This paper describes the preparation of monomethyl- and monoethylthallium derivatives by using thallic acetate and some methyl- and ethyltin compounds *in the absence of the halide anions other than fluoride**.

RESULTS AND DISCUSSION

We have isolated methyl- or ethyl(cyano)thallium acetate** by using a methyltin or ethyltin compound, such as $(CH_3)_2SnF_2$, $(CH_3)_3SnOAc$, $(CH_3)_4Sn$ or $(C_2H_5)_4Sn$, together with thallic acetate and sodium cyanide. The reactions of some methyltin

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* Monomethyl- or monoethylthallium dicarboxylates were found to be decomposed by treatment with chloride, bromide or iodide anions but not with fluoride anions[1,7].

** Methyl(cyano)thallium acetate can easily be derivatized to monomethylthallium oxide[8] by KOH or to monomethylthallium bis(*N*,*N*-dialkyldithiocarbamates)[9] by $KSSCNR_2$, and similarly ethyl(cyano)thallium acetate can be converted to monoethylthallium bis(*N*,*N*-dialkyldithiocarbamates)[9].

derivatives with thallic acetate in the absence of cyanide anion were also investigated (Table 1). From Table 1 it is seen that the monomethylthallium species was produced in fairly good yields in the early stage of the reaction, but the yield of dimethylthallium cation increased with time or when the mole ratio of CH_3/Tl employed was greater than unity (*e.g.* when the mole ratio, Sn/Tl = 1). These facts suggest that the methylation of thallium probably proceeds in two steps, *i.e.* via the formation and alkylation of the monomethylthallium species. However, in the preparation of $CH_3Tl(CN)OAc$ with $(CH_3)_3SnOAc$, which is similar to the reaction of $[CH_3SiF_5]^{2-}$ with the $Tl(OAc)_3/NaCN$ system[3], further methylation of the monomethylthallium species to the dimethylthallium cation is retarded, since in this case the monomethylthallium species was produced in higher yield than the dimethylthallium one even after 24 h. Probably this is a consequence of the appreciable covalent character of the Tl–CN bond in $CH_3Tl(CN)OAc$, with an apparent formation of a stable C–Tl–C configuration[8,11]. This conclusion is also in agreement with the fact that $CH_3Tl(CN)OAc$ is methylated by $(CH_3)_2SnF_2$ less readily than $CH_3Tl(OAc)_2$.

TABLE 1

METHYLATION OF THALLIC ACETATE WITH SOME METHYLTIN COMPOUNDS

Methyltin compounds	Concn. (mole/l)	Mole ratio (Sn/Tl)	Solvent	Product (%) after			
				3 h		24 h	
				CH_3Tl^{2+}	$(CH_3)_2Tl^+$	CH_3Tl^{2+}	$(CH_3)_2Tl^+$
$(CH_3)_4Sn$	0.333	1	CH_3OH	70	28	26	62
	0.083	1/4	CH_3OH	59	0		
$(CH_3)_3SnOAc$	0.250	1	CH_3OH	78	8	44	52
	0.250	1/3	CH_3OH	61	0		
$(CH_3)_2SnF_2$	0.250	1	H_2O	56	8	0[a]	20[a]
	0.250	1/2	H_2O	43	0		

[a] Most of the monomethylthallium species seems to be decomposed in an aqueous solution to give CH_3OH and CH_3COOCH_3, as indicated by the PMR spectrum (cf. Ref. 10).

EXPERIMENTAL

All the reactions were carried out at room temperature. The yields of the monomethylthallium and dimethylthallium species were calculated by making use of PMR spectroscopy with reference to a known amount of tertiary butanol as an internal standard.

Thallic acetate was a commercial product.

The IR and PMR spectra were measured using a Hitachi EPI-L spectrophotometer equipped with gratings (700–200 cm^{-1}) and a Japan Electron Optics JNM-3H-60 spectrometer, respectively.

Preparation of methyl(cyano)thallium acetate

To a methanol solution (7 ml) of $Tl(OAc)_3$ (3.8 g; 10 mmoles) and NaCN (0.5 g; 10 mmoles) in 2 ml of water was added $(CH_3)_3SnOAc$ (2.2 g; 10 mmoles) in methanol (25 ml). After standing for 24 h the white crystals obtained were recrystallized from methanol to give 1.20 g of this compound (39%), the IR and PMR spectra of which were identical with those of an authentic sample[8]. The PMR spectrum of the filtrate showed peaks due to the monomethylthallium species (approximately 18%) and a lesser amount of the dimethylthallium one (approximately 9%).

A similar method was employed in the reaction of tetramethyltin with thallic acetate and sodium cyanide, the yields of $CH_3Tl(CN)OAc$ being 33%. An analogous reaction of dimethyltin difluoride with thallic acetate and sodium cyanide in an aqueous solution gave 41% of $CH_3Tl(CN)OAc$.

Preparation of ethyl(cyano)thallium acetate

A methanol solution (5 ml) of $Tl(OAc)_3$ (3.8 g; 10 mmoles) and 15 ml of methanol containing 10 mmoles of tetraethyltin were mixed. After 4 h an aqueous solution (1 ml) of NaCN (0.3 g; 0.7 mmole) was added drop by drop to the reaction mixture. The white crystals obtained were recrystallized from methanol to give 1.20 g of this compound (36%); m.p. 144–145°. (Found: C, 18.82; H, 2.65; N, 4.20. $C_5H_8NO_2Tl$ calcd.: C, 18.86; H, 2.53; N, 4.40%.)

The reaction of methyltin compounds with $Tl(OAc)_3$

A methanol or aqueous solution of $Tl(OAc)_3$ and that of the methyltin compound in the same solvent (total amount about 2–3 ml) were mixed and after 3 h and 24 h the PMR spectra were measured at 20°. The results are shown in Table 1.

The reaction of $(CH_3)_2SnF_2$ with $CH_3Tl(OAc)_2$ or $CH_3Tl(CN)OAc$

An aqueous solution (1 ml) of $(CH_3)_2SnF_2$ (40 mg; 0.2 mmole) was added to $CH_3Tl(CN)OAc$ (64 mg; 0.2 mmole) in water (1 ml). The yields of the dimethylthallium species were 0% after 3 h and 24% after 24 h (from PMR). The reaction between $(CH_3)_2SnF_2$ and $CH_3Tl(OAc)_2$ was carried out similarly, the yields of the dimethylthallium species being 42% and 66% after 3 h and 24 h, respectively.

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