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(CHLOROMETHYL)THALLIUM(III) COMPOUNDS

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SUMMARY

Aryl(chloromethyl)thallium chlorides, $Ar(ClCH_2)TlCl$ ($Ar = C_6H_5$, p-$CH_3C_6H_4$) have been prepared by treatment of arylthallium dichlorides with diazomethane. The derived carboxylates, $Ar(ClCH_2)TlX$, react with HgX_2 to give the dicarboxylates, $(ClCH_2)TlX_2$ ($X = OCOCH_3$, $OCOC_3H_7$-i) and with tetramethyltin to give $CH_3(ClCH_2)TlX$ compounds. $R(ClCH_2)TlX$ compounds ($R = CH_3$, C_6H_5, p-$CH_3C_6H_4$) undergo disproportionation in methanol to R_2TlX and $(ClCH_2)_2TlX$ compounds.

INTRODUCTION

Halomethyl compounds of metals have been extensively studied[1-3]. However, as far as such derivatives of thallium are concerned, the only example is bis(chloromethyl)thallium chloride[4], an explosive solid prepared from the reaction of thallium trichloride and diazomethane. We describe below the preparation and properties of ten new (chloromethyl)thallium(III) compounds, of the types $R(ClCH_2)TlX$ and $(ClCH_2)TlX_2$, as shown in Table 1.

DISCUSSION

Aryl(chloromethyl)thallium(III) compounds can be obtained easily by treatment of monoarylthallium dichlorides with diazomethane.

$$ArTlCl_2 + CH_2N_2 \rightarrow Ar(ClCH_2)TlCl$$
$$Ar = C_6H_5,\ p\text{-}CH_3C_6H_4$$

This reaction proceeds smoothly at room temperature and the yields are almost quantitative. This is understandable, since the reaction involves the formation of the $C\text{–}Tl^+\text{–}C$ configuration, well-known to be stable[5,6]. By treatment with thallium(I) carboxylates, the chlorides can be converted into the carboxylates. The aryl groups in these aryl(chloromethyl)thallium carboxylates can be abstracted by mercuric carboxylates, as reported[7,8] for diorganothallium carboxylates.

$$Ar(ClCH_2)TlOCOR' + Hg(OCOR')_2 \rightarrow (ClCH_2)Tl(OCOR')_2 + ArHgOCOR'$$
$$R' = CH_3,\ i\text{-}C_3H_7$$

The (chloromethyl)thallium dicarboxylates thus obtained can be methylated with tetramethyltin, as can monoorganothallium dicarboxylates[9].

$$(ClCH_2)Tl(OCOR')_2 + (CH_3)_4Sn \rightarrow$$
$$\rightarrow CH_3(ClCH_2)TlOCOR' + (CH_3)_3SnOCOR'$$

TABLE 1

PROPERTIES OF (CHLOROMETHYL)THALLIUM DERIVATIVES, $R(ClCH_2)TlX$

R	*X*	*M.p.* (°C)	*Analysis found (calcd.) (%)*		
			C	*H*	*Cl*
C_6H_5	Cl	>300	22.56 (22.95)	1.87 (1.93)	18.96 (19.35)
	$OCOCH_3$	>180	28.08 (27.72)	2.58 (2.58)	9.14 (9.09)
	$OCOC_3H_7$-i	>200	31.68 (31.60)	3.33 (3.38)	7.92 (8.48)
p-$CH_3C_6H_4$	Cl	265–266	25.50 (25.26)	2.50 (2.39)	
	$OCOCH_3$	185	29.43 (29.73)	3.01 (2.99)	
	$OCOC_3H_7$-i	195	33.21 (33.36)	3.71 (3.73)	
CH_3	$OCOCH_3$	148–149	14.65 (14.65)	2.56 (2.46)	10.50 (10.81)
	$OCOC_3H_7$-i	149–150	20.00 (20.24)	3.52 (3.40)	9.80 (9.96)
$OCOCH_3$	$OCOCH_3$	132–133	16.29 (16.15)	2.19 (2.17)	9.34 (9.53)
$OCOC_3H_7$-i	$OCOC_3H_7$-i	153–155	25.54 (25.26)	3.91 (3.77)	7.89 (8.28)

TABLE 2

RELEVANT INFRARED FREQUENCIES (cm^{-1}) IN NUJOL MULLS AND SPIN–SPIN COUPLING CONSTANTS (Hz) OF (CHLOROMETHYL)THALLIUM COMPOUNDS, $R(ClCH_2)TlX$ IN CD_3OD

R	*X*	$\rho(Tl\text{–}CH_2)$	$\nu(Tl\text{–}C)$	$J(Tl\text{–}CH_2)$	$\tau(CH_2)$[d]
C_6H_5	Cl	[a]	493 w[b]	266[c]	6.08[c]
	$OCOCH_3$	[a]	508 w[b]	229	6.14
	$OCOC_3H_7$-i	[a]	514 m[b]	229	6.15
p-$CH_3C_6H_4$	Cl	731 s	498 w[b]	[e]	[e]
	$OCOCH_3$	725 m (br)	514 m[b]	230	6.05
	$OCOC_3H_7$-i	728 (sh)	512 m[b]	224	6.12
CH_3	$OCOCH_3$	732 (sh)	537 s	207	6.31
	$OCOC_3H_7$-i	732 (sh)	533 s	207	6.30
				187[f]	6.22[f]
$OCOCH_3$	$OCOCH_3$	738 s	515 w	487	5.70
$OCOC_3H_7$-i	$OCOC_3H_7$-i	725 (sh)	505 w	451	5.78

[a] Obscured by the absorption due to the phenyl group. [b] Additional bands due to the phenyl and p-tolyl groups are observed near 445 and 475 cm^{-1}, respectively. [c] In DMSO-d_6. [d] Relative to internal TMS (τ 10 ppm). [e] Cannot be detected in DMSO because of limited solubility. [f] In chloroform.

All these organo(chloromethyl)thallium carboxylates readily undergo disproportionation in methanol at room temperature:

$$2\,R(ClCH_2)TlOCOR' \rightleftarrows R_2TlOCOR' + (ClCH_2)_2TlOCOR'$$

$$R = CH_3,\ C_6H_5,\ p\text{-}CH_3C_6H_4\ ;\ R' = CH_3,\ i\text{-}C_3H_7$$

In the case of $CH_3(ClCH_2)TlOCOR'$, the equilibrium constant was determined from the PMR spectrum, and reveals that the equilibrium lies towards the unsymmetrical diorganothallium compound.

Features of the IR and PMR spectra of the (chloromethyl)thallium compounds are shown in Table 2.

EXPERIMENTAL

Preparation of $C_6H_5(ClCH_2)TlCl$

To a methanol solution (50 ml) of $C_6H_5TlCl_2$ (6 g, 17 mmol) was added diazomethane (0.75 g, 17 mmol) in ether. Immediate gas evolution occurred, and a white precipitate formed. The precipitate was separated to give $C_6H_5(ClCH_2)TlCl$ (4.5 g, 72%). The compound $p\text{-}CH_3C_6H_4(ClCH_2)TlCl$ was prepared analogously from $p\text{-}CH_3C_6H_4TlCl_2$ and diazomethane.

$Ar(ClCH_2)TlCl$ and an equimolar amount of thallium(I) carboxylate were stirred for 3 h in methanol. The filtrate was allowed to evaporate slowly to give needles of $Ar(ClCH_2)TlOCOR'$.

Preparation of $(ClCH_2)Tl(OCOC_3H_7\text{-}i)_2$

$C_6H_5(ClCH_2)TlOCOC_3H_7\text{-}i$ (1.25 g, 3 mmol) and mercuric isobutyrate (1.1 g, 3 mmol) were dissolved in 20 ml of methanol and the solution was allowed to stand for 3 h. The solid obtained by vacuum evaporation was washed with 300 ml of benzene. The remaining white solid was recrystallised from methanol to give 0.78 g (61%) of $(ClCH_2)Tl(OCOC_3H_7\text{-}i)_2$. (Chloromethyl)thallium diacetate was obtained analogously from $C_6H_5(ClCH_2)TlOCOCH_3$ and $Hg(OCOCH_3)_2$.

Preparation of $CH_3(ClCH_2)TlOCOC_3H_7\text{-}i$

(Chloromethyl)thallium diisobutyrate (0.86 g, 2 mmol) and tetramethyltin (0.36 g, 2 mmol) was dissolved in 30 ml of methanol, and the mixture was set aside for 3 h at room temperature. After evaporation of the solution, 200 ml of diethyl ether was added to the residual solid. Soluble trimethyltin isobutyrate was removed by filtration, and the remaining white solid was recrystallised from methanol or chloroform/petroleum ether to give 0.5 g (70%) of $CH_3(ClCH_2)TlOCOC_3H_7\text{-}i$

Redistribution of $CH_3(ClCH_2)TlOCOC_3H_7\text{-}i$

The PMR spectra of $CH_3(ClCH_2)TlOCOC_3H_7\text{-}i$ in CD_3OD were recorded over a period of 3 h at room temperature. The intensities of the peaks due to $(C\underline{H}_3)_2Tl$ (J 425, τ 8.98) and $(ClC\underline{H}_2)_2Tl$ (J 224, τ 6.18) increased during this time to a constant value. On addition of $(CH_3)_2TlOCOC_3H_7\text{-}i$, the intensities of the peaks due to $C\underline{H}_3(ClC\underline{H}_2)Tl$ again increased. The equilibrium constant, K, was determined by calculating the peak areas with reference to cyclohexane as internal standard, and found to have a value of 0.1. In the case of $Ar(ClCH_2)TlOCOR'$ compounds, determination of the equilibrium constant by PMR measurement is difficult, but the occurrence of the redistribution was confirmed by the infrared spectra of the halides prepared from the carboxylate mixtures.

REFERENCES

1 D. Seyferth, *Chem. Rev.*, 55 (1955) 1155.
2 D. Seyferth and S. B. Andrews, *J. Organometal. Chem.*, 30 (1971) 151 and references therein.
3 M. F. Lappert and J. S. Poland, *Advan. Organometal. Chem.*, 9 (1970) 397.
4 A. Ya. Yakubovich and N. A. Ginsberg, *Dokl. Akad. Nauk SSSR.*, 73 (1950) 957; *Chem. Abstr.*, 47 (1951) 2857.
5 H. Kurosawa and R. Okawara, *Organometal. Chem. Rev., Sect. B*, 6 (1970) 65.
6 A. G. Lee, *The Chemistry of Thallium*, Elsevier, London, 1971.
7 H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 10 (1967) 211.
8 T. Abe, H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 25 (1970) 353.
9 M. Tanaka, H. Kurosawa and R. Okawara, *J. Organometal. Chem.*, 18 (1969) 49.