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Synthesis and Unusual Properties of Trimethylsilylmethyl, Neopentyl, and Related Alkylthallium Compounds

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Synthesis of some new trimethylsilylmethyl, neopentyl, and isobutylthallium compounds is described. Dialkylthallium halides containing these bulky alkyl substituents were found to be dimeric, in marked contrast to the polymeric dimethylthallium halide analogs. Trimethylsilylmethylthallium diisobutyrate possesses much higher stability than the methyl and ethylthallium analogs. These facts were discussed in terms of the steric bulk of the alkyl groups attached to thallium.

Organometallic compounds containing the trimethylsilylmethyl or neopentyl groups are of current interest because of abilities of these groups to apparently stabilize metal–carbon bonds.1) Of particular importance in considering factors which affect kinetic stabilities and structural aspects of such a class of organometallic compounds is clearly bulkiness of the alkyl groups. We wish to describe synthesis of some new organothallium compounds containing bulky alkyl substituents whose unique properties may be contrasted with those of common, less bulky alkyl derivatives of thallium.2)

Experimental

The infrared spectra were run on a Hitachi 225 or EPI-2G grating spectrophotometer. The ^{1}H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer. Molecular weights were determined in $CHCl_3$ at 25 °C using a Mechlorab vapor pressure osmometer Model 302. Tetrahydrofuran for the preparation of the Grignard and lithium reagents was dried with $LiAlH_4$.

Preparation of New Compounds. *Dialkylthallium Chlorides*: R_2TlCl ($R=Me_3CCH_2$, Me_2CHCH_2) were prepared in a manner similar to that3) for obtaining $Pr^n{}_2TlCl$ from $TlCl_3$ and the appropriate Grignard reagents in tetrahydrofuran. Recrystallization from CH_2Cl_2 or $CHCl_3$ gave colorless needle-like crystals. *$(Me_3SiCH_2)_2TlCl$*: To a tetrahydrofuran solution (20 ml) of $TlCl_3$ (0.75 g; 2.4 mmol) was added lithiomethyltrimethylsilane,4) which was prepared from Me_4Si (2.0 g; 24 mmol), *N,N,N′,N′*-tetramethylethylenediammine (2.8 g; 24 mmol) and 15 ml of 1.5 M Bu^nLi in hexane. Immediately metallic thallium formed and the solution became black. After stirring for 2 h, the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride. The tetrahydrofuran extract was concentrated to give an oily product which was washed with water several times. Recrystallization from $CHCl_3$ gave white needles of $(Me_3SiCH_2)_2TlCl$ (0.34 g; 0.82 mmol). $(Me_3SiCH_2)_2TlBr$ was prepared from TlBr and Me_3SiCH_2Li in a similar manner. *$Me_3SiCH_2Tl(OOCPr^i)_2$*: Mercuric isobutyrate (0.30 g; 0.81 mmol) and $(Me_3SiCH_2)_2TlOOCPr^i$ (0.38 g; 0.81 mmol), which was prepared from $(Me_3SiCH_2)_2TlCl$ and $TlOOCPr^i$ in $CHCl_3$, were mixed in $CHCl_3$ (10 ml) at room temperature. The solid products obtained by vacuum evaporation of the solvent after 1 day were recrystallized from hexane to give 0.10 g (0.22 mmol) of $Me_3SiCH_2Tl(OOCPr^i)_2$. *$Me(Me_3SiCH_2)TlBr$*: Pyridinium perbromide (0.05 g; 0.19 mmol) and $(Me_3SiCH_2)_2TlCl$ (0.08 g; 0.19 mmol) were dissolved in 10 ml of $CHCl_3$. After 30 min tetramethyltin (0.04 g; 0.24 mmol) was added to the solution in order to methylate5) a monoalkylthallium species produced *in situ*. After 1 h the solution was filtered. The solid products obtained by vacuum evaporation of the filtrate were recrystallized from $CHCl_3$ to give 0.06 g (0.16 mmol) of $Me(Me_3SiCH_2)TlBr$. $Me(Me_3SiCH_2)TlOOCPr^i$ was prepared from $Me(Me_3SiCH_2)TlBr$ and $TlOOCPr^i$ in $CHCl_3$. Recrystallization from hexane gave fine needles of the compound.

Analytical data of the new compounds thus obtained are summarized in Table 1. Infrared and ^{1}H NMR spectral data of the representative trimethylsilylmethyl compounds are shown in Table 2.

Pyrolysis of $(Me_2CHCH_2)_2TlCl$. 100 mg (0.28 mmol) of a solid sample of $(Me_2CHCH_2)_2TlCl$ in a sealed tube under reduced pressure (10^{-1} mmHg) was heated at 170 °C for 3 h. Sixty-five mg (0.27 mmol) of white powdery TlCl remained in the tube, and GLC analysis of gaseous products indicated

TABLE 1. PROPERTIES AND ANALYTICAL DATA OF ORGANOTHALLIUM COMPOUNDS

	Compound[a)]	Mp (°C)	Found (Calcd) %C	Found (Calcd) %H	Mol wt Found (Calcd[b)])	Concn[c)]
1a	$R^1{}_2TlCl$	238	23.26 (23.20)	5.51 (5.35)	824 (828)	0.125
1b	$R^1{}_2TlBr$	234	21.53 (20.95)	5.24 (4.83)	920 (918)	0.152
2	$R^2{}_2TlCl$	>340	31.18 (31.43)	5.95 (5.80)	776 (762)	0.098
3	$R^3{}_2TlCl$[d)]	e)	26.68 (27.14)	5.16 (5.12)	718 (708)	0.196
4	MeR^1TlBr	231	15.38 (15.53)	3.76 (3.65)	751 (772)	0.073
5	$R^1{}_2TlOOCPr^i$	72	31.04 (30.94)	6.32 (6.27)		
6	$R^1Tl(OOCPr^i)_2$	144	30.94 (30.60)	5.63 (5.41)		
7	$MeR^1TlOOCPr^i$	176	27.37 (27.46)	5.36 (5.38)		

a) $R^1=Me_3SiCH_2$, $R^2=Me_3CCH_2$, $R^3=Me_2CHCH_2$. b) As dimer. c) Mol%. d) % Tl, Found, 57.40: Calcd, 57.72. e) No definite melting point.

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TABLE 2. RELEVANT INFRARED[a] AND ^{1}H NMR[b] SPECTRAL DATA OF TRIMETHYLSILYLMETHYLTHALLIUM COMPOUNDS

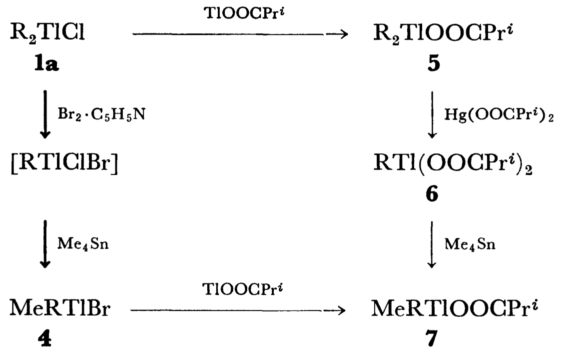
Compound[c]		ν(Tl-C)		$^2J_{\text{Tl-CH}_2}$	$^2J_{\text{Tl-CH}_3}$
1a	R_2TlCl	520	491	537	
1b	R_2TlBr	520	489	536	
4	MeRTlBr	528	464	539	342
5	$R_2TlOOCPr^i$	514	478	566	
7	$MeRTlOOCPr^i$	d)	488	562	376
6	$RTl(OOCPr^i)_2$	d)		1121	

a) In Nujol mulls. ν in cm^{-1}. b) In $CDCl_3$. J in Hz. c) $R=Me_3SiCH_2$. d) Obscured by the ligand absorptions.

the presence of only isobutane and isobutene in almost 1 : 1 mole ratio. Also, 0.4 ml of $CDCl_3$ was added to a residual mixture, while kept at −78 °C, after a separate pyrolysis run carried out under the identical condition. The ^{1}H NMR spectrum of this $CDCl_3$ solution again confirmed the formation of only isobutane and isobutene (1 : 1) as chloroform-soluble products. No indication of the presence of 2,5-dimethylhexane could be obtained through GLC and ^{1}H NMR analyses.

Results and Discussion

Synthetic Route. Dialkylthallium halides, $(Me_3SiCH_2)_2TlX$ (**1a** X=Cl; **1b** X=Br) and $(Me_2RCCH_2)_2TlCl$ (**2** R=Me; **3** R=H) were prepared using the appropriate lithium or the Grignard reagents. **1a** was further derivatized to other trimethylsilylmethyl compounds of thallium as outlined in Scheme 1.



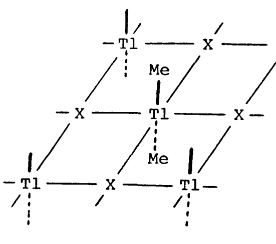
Scheme 1. $R=Me_3SiCH_2$.

Dialkylthallium Compounds. The trimethylsilylmethyl and neopentylthallium halides, **1a**, **1b**, **2**, and **4** possess good thermal stabilities comparable to those of dimethyl, diethyl or dipropyl analogs. However, interestingly, the diisobutylthallium derivative, **3** was found to be much less stable than not only **2** but Pr^n_2TlCl. Thus, even standing a crystalline sample of **3** at room temperature gradually caused decomposition to result in contamination of the sample with TlCl. Approximately 1 : 1 molar mixture of isobutane and isobutene was detected in the gaseous products from pyrolysis of the solid sample of **3** at 170 °C under reduced pressure for 3 h. 2,5-Dimethylhexane was not formed.

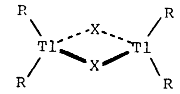
$$\underset{\mathbf{3}}{(Me_2CHCH_2)_2TlCl} \xrightarrow{\Delta} Me_3CH + Me_2C{=}CH_2 + TlCl$$

On the contrary, **2** and Pr^n_2TlCl were found to be totally stable under the same conditions. In view of this fact, it seems unlikely that the Tl–C bond strength in **3** is exceptionally weak. Although the precise mechanism of the decomposition of **3** yet remains to be elucidated, the presence of the labile β-methine hydrogen in the isobutyl group apparently is essential to the unique instability of this compound. In this regard, it should be mentioned that the removal of the β-methine hydrogen of the isobutyl group in $R(Me_2CHCH_2)Hg$ by a radical species promoted the liberation of isobutene and the homolytic fission of the Hg–R bond.[6]

Dimethylthallium halides are insoluble in non-coordinating solvents possibly due to the occurrence of the polymeric structure with a linear C–Tl–C unit lying perpendicular to the $(Tl–X)_n$ network as shown in **A** below.[7] It is well recognized[8] that the linear C–Tl–C configuration is energetically most favored in dialkylthallium compounds. On the contrary, **1**—**4** are all fairly soluble in $CHCl_3$ and benzene, and were found to be dimeric in $CHCl_3$ (Table 1) with a bent C–Tl–C configuration as suggested for **1a** and **1b** by the appearance of two TlC_2 stretching modes (Table 2).



A (X=Cl, Br, I)



B ($R=Me_3SiCH_2$, Me_3CCH_2, Me_2CHCH_2; X=Cl, Br)

However, Pr^n_2TlCl was too insoluble to determine its molecular weight. We assume that a part of the reasons for the increased solubilities of **1**—**4**, compared to those of Me_2TlX and Pr^n_2TlCl, is steric; the steric bulk of the alkyl groups in **1**—**4** may have precluded the formation of the polymeric network with the Tl-X interaction as strong as that in $(Me_2TlX)_n$, as will be explained below. Thus, in molecular models for **1**, **2**, and **4** having a hypothetical structure similar to **A**, it is almost impossible to attach the Me_3SiCH_2 or Me_3CCH_2 groups, totally free of steric constraint, to each thallium atom in the $(Tl–X)_n$ layer which was constructed assuming the Tl–X bond length equal to that[7] in $(Me_2TlX)_n$. The most dominant repulsions observed in such models are those between the β-methyl substituents of one alkyl group and the CH_2 protons of the nearest alkyl or those between the former and the halogen atoms There exist similar kinds of, though to a lesser extent, steric repulsions in the similar model structure for **3**, while such model for Pr^n_2TlCl can now be readily constructed free of constraints without elongating the Tl–Cl distance found in $(Me_2TlCl)_n$.

A brief comparison of the electronic effects of the Me_3SiCH_2 and Me groups can be made on the basis of ^{1}H NMR spectral data. As shown in Table 2, $J_{\text{Tl-CH}_2}$ and $J_{\text{Tl-CH}_3}$ values of **7** are almost the same as those of **5** and $Me_2TlOOCPr^i$(377 Hz)[9], respectively.

Similarly, $J_{\mathrm{Tl-CH_2}}$ value of **1b** is very close to that of **4**. In view of the proposition[10)] that thallium-proton spin-spin coupling constant is dominated by Fermi contact term, the results shown above suggest a similarity in the ability of the Me_3SiCH_2 and Me groups to affect the s-character in the bonds between thallium and these groups. A similar trend was also reported[11)] that trans influences of the two groups are comparable in square planar Pt^{II} complexes.

Monoalkylthallium Compounds. It should be noted that **6** is much more stable than its methyl or ethyl analogs. Thus, for example, **6** can be recovered unchanged from hot methanol or dimethyl sulfoxide, while the latter two readily decomposed under the similar conditions to give thallium isobutyrate and $ROOCPr^i$ (R=Me, Et).[9)] Kinetic studies on the similar decomposition of $MeTl(OAc)_2$ indicated the reaction to proceed through the nucleophilic attack of the acetate anion at the methyl carbon.[12)] Therefore, the bulkiness of the Me_3SiCH_2 group almost certainly depresses the approach of a nucleophile at the α-carbon in **6**. A much higher stability of $PhCH(OMe)CH_2TlCl_2$[13)] or a mononeopentylthallium halide species[14)] than $MeTlX_2$ (X=Cl, Br) was also interpreted on similar grounds, although no detailed description on the isolation of the neopentyl derivative has yet appeared since its preliminary publication.

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