

## Interaction Products of Diphenylthallium(III) Compounds with Mercury(II) salts

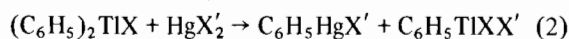
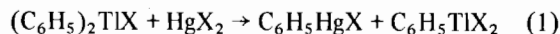
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Received April 30, 1976

Workers have employed the interaction of mercury(II) salts with organometallic compounds for cleavage of organic groups.<sup>1</sup> Such reactions have not been investigated with organothallium compounds. Kurosawa and Okawa<sup>2,3</sup> however, employed the reaction of dialkylthallium(III) acetate with mercury(II) acetate to obtain alkylthallium(III) diacetate. In continuation to our studies on diarylthallium(III) derivatives,<sup>4-7</sup> we now report more than half a dozen interactions of these with mercury(II) salts resulting in the cleavage of phenyl group which provides a convenient method for synthesising compounds of the type  $C_6H_5TlX_2$  or  $C_6H_5TlXX'$  ( $X$  = an anion,  $XX'$  = two different species of anions) as per equations below:



The compounds have been characterised by elemental analyses and I.R. data.

## Experimental

### Materials

Diphenylthallium(III) derivatives<sup>8,9</sup> were prepared according to the literature methods. Other reagents of analytical grade (BDH/S. Merk) were used without further purification.

### Method A

In a typical reaction, 2 mmol of diphenylthallium(III) derivatives and equimolar amount of suitable mercury(II) salt in dry methanol (acetone or 1:1 acetone-ethanol mixture for  $PhTlCl_2$ ) were refluxed for 3-4 hours and filtered hot. The clear solution on crystallisation yielded organomercurial(II) compounds in 65-90% yield.

The mother liquor was evaporated to dryness under reduced pressure and the resulting solid, on extraction with hot water or chloroform gave the desired symmetric or the hitherto unknown asymmetric derivatives of phenylthallium(III) which were dried under vacuum.

### Method B

Equimolar amounts (2mmol) of diphenylthallium(III) derivative and suitable mercury(II) salt were dissolved in 100-150 ml of warm dry methanol and the solution was allowed to stand for 8-20 hours with occasional shaking. The solution was then evaporated under reduced pressure and the solid was extracted with benzene to isolate the organomercury(II) compounds. The residual solid on crystallisation from water-methanol mixture (1:1) yielded phenylthallium(III) derivatives. Phenylthallium(III) diacetate was extracted with chloroform.

The elemental analyses were done by micro-analytical methods with certain modifications and thallium was estimated as  $Tl_2CrO_4$  from  $H_2SO_4$ - $HNO_3$  digested samples.<sup>10</sup>

Melting points, analytical and conductometric data of the compounds are presented in Table I. Experimental data of the known compounds, phenylthallium(III) dichloride, dicyanide and diacetate are omitted. Organomercurials were also characterised but the data are not reported here as the compounds are well studied.

Generally the compounds are white crystalline solids, insoluble in common organic solvents such as benzene, petroleum ether, diethyl ether *etc.* but appreciably soluble in pyridine, dimethylformamide, dimethylsulphoxide, water-ethanol mixture and water. They melt above 200 °C. Molar conductance of  $10^{-3}$  M solutions measured in methanol using a Philips conductivity bridge type PR 9500 having a dip-type conductivity cell at 35 °C was found to be in the range of 31.5-55.3  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , indicating electrolytic nature of the compounds.

The infrared spectra of the compounds in nujol were recorded in the region of 4000-200  $\text{cm}^{-1}$ . Melting points of the compounds were determined on electrically operated apparatus (M/s. Teshniwal and Brothers, Bombay, India).

The infrared absorptions associated with the aromatic group are observed at the positions reported by us in one of our earlier publications<sup>5</sup> and are not listed here. The absorptions associated with various modes of cyanide, isothiocyanate and nitrate groups are discussed.

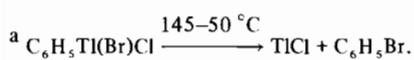
## Results and Discussion

### Spectra of Pseudohalide Derivatives (Cyanides)

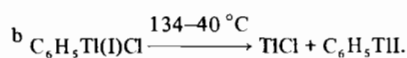
Coates and Mukherjee<sup>11</sup> observed the  $C\equiv N$  stretch as a single band at 2101  $\text{cm}^{-1}$  in dimethylthallium(III) cyanide as compared to the absorptions at  $2200 \pm 25 \text{ cm}^{-1}$  for the corresponding analogue of the other group III metals. This stretch in the spectra of dicyanide and chloro-cyanide derivatives of phenylthallium(III) appears at  $2108 \pm 2 \text{ cm}^{-1}$  as a

TABLE I. Experimental Data for Phenylthallium(III) Diderivatives.

Compound (Method)	M.P. °C	Analytical Data, found (calcd.)%				Mol. Cond. in Methanol (Concn. 10 <sup>-3</sup> M)
		Tl	C	H	N	
C <sub>6</sub> H <sub>5</sub> Tl(Br)Cl (A)	a	51.6 (51.4)	18.2 (18.1)	1.2 (1.2)	— —	32.4 (1.2)
C <sub>6</sub> H <sub>5</sub> Tl(I)Cl (A)	b	45.9 (46.0)	16.5 (16.2)	1.2 (1.1)	— —	31.5 (1.0)
C <sub>6</sub> H <sub>5</sub> Tl(CN)Cl (B)	253–5	59.2 (59.5)	24.4 (24.5)	1.5 (1.4)	4.3 (4.1)	34.5 (1.0)
C <sub>6</sub> H <sub>5</sub> Tl(NCS)Cl (B)	203d	54.1 (54.4)	22.6 (22.4)	1.2 (1.3)	3.6 (3.7)	34.6 (1.0)
C <sub>6</sub> H <sub>5</sub> Tl(NO <sub>3</sub> )Cl (B)	222–31	54.0 (53.9)	19.2 (19.0)	1.4 (1.3)	3.5 (3.7)	55.3 (1.3)



d = decomposition.



sharp band of weak to medium intensity and close to the C≡N absorption for sodium (2085 cm<sup>-1</sup>) and potassium (2076 cm<sup>-1</sup>)<sup>11</sup>. The absorption and the fact that these are ionised in methanol support their ionic nature.

#### Chloro-iso-thiocyanate Derivative

Reported I.R. data of various isothiocyanates<sup>12,13</sup> place the asymmetric NCS stretching at 2075 ± 35 and the corresponding vibration of thiocyanate at 2155 ± 15 cm<sup>-1</sup>. This absorption in phenylthallium(III) chloro-isothiocyanate we have observed at 2060 cm<sup>-1</sup> as a slightly broad band of very strong intensity, which is very close to the asymmetric NCS stretching absorption in solid potassium isothiocyanate at 2053 cm<sup>-1</sup>.<sup>14</sup> Shape, position and intensity suggest an iso-structure for the compounds having ionic character, which agrees with the conductance data.

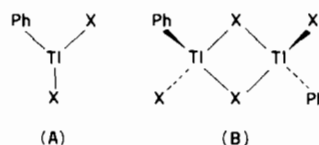
Symmetric NCS stretching and NCS bending mode have been identified, at 904 and 477 cm<sup>-1</sup>, respectively, as weak absorptions.

#### Chloro-Nitrate Derivative

In the spectrum of phenylthallium(III) chloronitrate, four absorptions of strong to weak intensity located at 1380, 1042, 808 and 705 cm<sup>-1</sup> are assigned to asymmetric stretching ν<sub>3</sub>, symmetric stretching ν<sub>1</sub>, bending ν<sub>2</sub> and planar rocking ν<sub>4</sub> modes of vibration of nitrate group respectively. The values are in the range reported for ionic nitrates<sup>15,16</sup> which support our conductance data. An absorption of weak intensity appeared at 1755 cm<sup>-1</sup> which may be attributed to a combination band denoted by ν<sub>1</sub> + ν<sub>4</sub>.

Besides the above, the absorptions associated with Tl-Cl stretches have also been identified in the spectra of the compounds in the range of 342 to 330 cm<sup>-1</sup>. In accordance with previous observation,<sup>17</sup>

two absorptions at 342 and 333 cm<sup>-1</sup> as bands of medium intensity suggest a probability of a monomeric structure (A) for PhTlCl<sub>2</sub> in the solid state and not a dimeric structure (B).



In other di-derivatives of phenylthallium(III), I.R. data could not be used for throwing light on structure because the compound had only one Tl-Cl band. Stretches associated with Tl-Br and Tl-I fall beyond the recorded range of the spectra.

#### Acknowledgments

We are thankful to the Head of the Chemistry Department, Lucknow University, for facilities and to the C.S.I.R., New Delhi, for financial support. The authors are also grateful to Prof. T. N. Srivastava (Lucknow University) for interesting discussions and suggestions.

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