REACTION OF ASYMMETRIC ORGANOMERCURY COMPOUNDS
WITH THALLIUM TRICHLORIDE

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We had observed a difference in the exchange rates of the cis- and trans-β-chlorovinyl groups when cis-trans-bis(β-chlorovinyl)mercury is reacted with thallium trichloride [1]. It was also established that the trans-isomers of organometallic compounds containing an olefinic hydrocarbon radical react with thallium trichloride and tribromide much more rapidly than do the cis-isomers [2, 3]. If it is assumed, as we had done with a substantial degree of certainty, that replacement of metal by metal is accomplished as the result of electrophilic attack by the metal halide on the radical of the asymmetric compound, then it follows that the radicals of trans-structure are more electronegative and in the Kharasch series are located to the left of their cis-isomers. It seemed of undoubted interest to expand the study of behavior in the reaction with TICl3 to a wider orbit of asymmetric organomercury compounds for the purpose of comparing a series of radicals, arranged in the order of their ease of cleavage in this reaction, with the Kharasch series, where the hydrogen ion serves as the radical-cleaving reagent.

For this purpose we synthesized a series of asymmetric organomercury compounds, starting with the organolithium [4] and organomagnesium [5] compounds and employing the method developed by Nesmeyanov, Kocheshkov, and Freidlina [6], and investigated their exchange reaction with thallium trichloride, proceeding in accordance with the scheme:

\[ 2R'HgR' + TICl_3 \rightarrow R_2TICI + 2R'HgCl \]

Analogous to cis-trans-bis(β-chlorovinyl)mercury [1], cis-trans-dipropenylmercury reacts with thallium trichloride to yield only the trans-dipropenylthallium chloride in 93% of the theoretical yield, with none of the cis-isomer as impurity, while the cis-propenyl radical remains attached to the mercury atom as cis-propenylmercury chloride:

<table>
<thead>
<tr>
<th>Formula of starting compound</th>
<th>Reaction products isolated</th>
<th>Organothallium compound</th>
<th>Organomercury compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H5HgCl</td>
<td>C6H5HgCl</td>
<td>(C6H5)2TICI</td>
<td>(α-C6H5H5)TICI</td>
</tr>
<tr>
<td>C6H5HgC6H5</td>
<td>C6H5HgCl</td>
<td>(α-C6H5H5)TICI</td>
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<td>(α-C6H5H5)TICI</td>
<td>(α-C6H5H5)TICI</td>
</tr>
<tr>
<td>o-Ch2OC6H4HgC6H5</td>
<td>o-Ch2OC6H4HgC6H5</td>
<td>(α-C6H5H5)TICI</td>
<td>(α-C6H5H5)TICI</td>
</tr>
<tr>
<td>(CH2)3C6H5HgCl</td>
<td>(α-C6H5H5)TICI</td>
<td>(α-C6H5H5)TICI</td>
<td>(α-C6H5H5)TICI</td>
</tr>
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</tr>
</tbody>
</table>
The cases observed by us earlier by reacting asymmetric organomercury compounds, containing stereoisomeric olefin radicals, with thallium trichloride have been summarized in one table along with the experimental material described in this paper.

As a result, study revealed that thallium trichloride exchanges two of its chlorine atoms for those radicals attached to the mercury atom that are subjected to electrophilic attack by the hydrogen ion in the decomposition of RHgR' with hydrochloric acid [7], with the exception of phenyl-α-naphthylmercury, which deviates from this rule.

**EXPERIMENTAL**

The reaction of cis-trans-dipropenylmercury with thallium trichloride was described in a previous paper [4].

**Reaction of ethylphenylmercury with thallium trichloride.** With cooling (ice + water), 2.5 g (0.008 mole) of thallium trichloride in ether solution was added to 5 g (0.016 mole) of ethylphenylmercury in ether. The obtained precipitate was filtered, washed with ether, and then with acetone. After recrystallization from pyridine, the obtained diphenylthallium chloride did not melt up to 310°; weight 2.35 g (75% of theory). Found: C 37.20, 37.08; H 2.64, 2.58%. C_{12}H_{10}TlCl. Calculated: C 36.57; H 2.56%.

**Reaction of ethyl-α-naphthylmercury with thallium trichloride.** With cooling, a solution of 2 g (0.0056 mole) of ethyl-α-naphthylmercury in 50 ml of absolute ether was mixed with an ether solution of 1.72 g (0.0027 mole) of thallium trichloride. After 30 min the ether was removed by distillation, and the residue was boiled with water. The hot aqueous solution was separated from the precipitate, which after recrystallization from benzene had m. p. 188-189°; weight 0.4 g (64.5%). The mixed melting point with authentic α-naphthylmercury chloride was not depressed. From the aqueous solution we isolated 0.38 g (62.3%) of phenylthallium dichloride with m. p. 240-242°. According to the literature [8]: m. p. 240°.

**Reaction of phenyl-α-anisylmercury with thallium trichloride.** a) With cooling, a solution of 0.7 g (0.0017 mole) of phenyl-α-anisylmercury in 30 ml of absolute ether was mixed with an ether solution of 0.537 g (0.0017 mole) of thallium trichloride. After 30 min the ether was removed by distillation, and the residue was boiled with water. The hot aqueous solution was separated from the precipitate, which after recrystallization from benzene had m. p. 188-189°; weight 0.4 g (64.5%). The mixed melting point with authentic α-naphthylmercury chloride was not depressed. From the aqueous solution we isolated 0.38 g (62.3%) of phenylthallium dichloride with m. p. 240-242°. According to the literature [8]: m. p. 240°.

b) A solution of 1.3 g (0.0032 mole) of phenyl-α-anisylmercury in 25 ml of dry dioxane was mixed with an ether solution of 0.61 g (0.0019 mole) of thallium trichloride. The next day the obtained precipitate of diphenylthallium chloride was filtered, washed with ether, and dried. After recrystallization from pyridine it decomposed at 310°; weight 0.5 g (79.3%). Found: C 36.41, 36.57; H 2.61, 2.63%. C_{15}H_{16}TlCl. Calculated: C 36.57; H 2.56%.

**Reaction of α-naphthyl-o-anisylmercury with thallium trichloride.** A solution of 0.63 g (0.0014 mole) of α-naphthyl-o-anisylmercury, m. p. 223-225°, in 20 ml of dry dioxane was mixed at 40° with an ether solution of 0.22 g (0.0007 mole) of thallium trichloride. The next day the dioxane was distilled off using a water-jet pump. The remaining solid residue (0.8 g) was treated with hot alcohol. Here the insoluble portion of the precipitate was distilled off using a water-jet pump. The mixed melting point with authentic α-naphthylmercury chloride was not depressed. From the alcohol solution we isolated α-naphthylmercury chloride with m. p. 188-189°; weight 0.44 g (86.27%).