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Abstract

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A NEW METHOD FOR THE SYNTHESIS OF ORGANOTHALLIUM COMPOUNDS OF THE CLASS $ArTlX_2$

A substantial gap in the chemistry of organothallium compounds is the absence of reliable methods of preparation and, consequently, the low availability and insufficient study of the class $ArTlX_2$.

Indeed, Challenger's method (^{1}) (via organoboron compounds) is multistage and, moreover, leads to $ArTlX_2$ (where X = halogen), i.e., to a class of compounds prone to secondary processes:

$$2RTlCl_2 \rightleftarrows R_2TlCl + TlCl_3 \rightarrow Tl_2Cl_4 + 2RCl.$$

Thus, Nametkin, Mel'nikov, and Gracheva (^{2}), following Challenger or using the "reverse disproportionation" reaction (^{3}), because of the side reactions described above, described $ArTlX_2$ (X = halogen) as substances colored yellow, orange, and brown, whereas in reality they are colorless (see below).

In the present work we describe for the first time a method for preparing $ArTlX_2$ (X = residue of an organic acid), using salts of organic acids of trivalent thallium* in reaction with organomercury compounds:

$$(C_6H_5)_2Hg + Tl[OOC \cdot CH(CH_3)_2]_3 \rightarrow$$
$$\rightarrow C_6H_5Tl[OOC \cdot CH(CH_3)_2]_2 + C_6H_5HgOOCCH(CH_3)_2. \qquad (1)$$

The reaction, which proceeds rapidly at room temperature in a chloroform medium, gives, in good yields, compounds of the class $ArTl(OOCR)_2$ that crystallize excellently. Compounds of this kind are stable, are not prone (in contrast to the corresponding halide compounds) to secondary transformations, and are colorless.

The reaction described in the literature (^{4}) between diphenylmercury and thallium trichloride, despite the favorable ratio of reagents (1 mole : 1 mole), has hitherto led only to $\mathrm{Ar_2TlX}$ (X = halogen).

By using salts of organic acids we can, at our discretion (depending on the molar ratios taken), direct the reaction according to equations (1) or (2):

$$\begin{gathered}2(\mathrm{C_6H_5})_2\mathrm{Hg} + \mathrm{Tl[OOCCH\cdot(CH_3)_2]_3} \rightarrow \\ \rightarrow (\mathrm{C_6H_5})_2\mathrm{TlOOC\cdot CH(CH_3)_2} + 2\mathrm{C_6H_5HgOOC\cdot CH(CH_3)_2},\end{gathered} \tag{2}$$

and, starting from the corresponding organomercury compounds, one can obtain organothallium compounds $\mathrm{ArTl(OOCR)_2}$ or $\mathrm{Ar_2TlOOCR}$ with substituents in the nucleus.

The compounds $\mathrm{ArTl(OOCR)_2}$ obtained by us are identical with the compounds synthesized by the direct thallation method developed by us (^{5}). Phenylthallium diisobutyrate, consequently, can be obtained from benzene and thallium triisobutyrate (yield 90%):

$$\mathrm{C_6H_6} + \mathrm{Tl[OOC\cdot CH(CH_3)_2]_3} \rightarrow \mathrm{C_6H_5Tl[OOC\cdot CH(CH_3)_2]_2} + \mathrm{(CH_3)_2CHCOOH}. \tag{3}$$

* In the present work we used salts of isobutyric acid; however, as experience shows, salts of other organic acids are also applicable.

The reaction, "reverse to disproportionation,"

$$(\mathrm{C_6H_5})_2\mathrm{TlOOC\cdot CH(CH_3)_2} + \mathrm{Tl[OOC\cdot CH(CH_3)_2]_3} \rightarrow 2\mathrm{C_6H_5[TlOOCCH(CH_3)_2]_2}, \tag{4}$$

which in our case proceeds in quantitative yield, also leads to colorless organothallium compounds.

Replacement of the organic-acid residue by a halide according to the equation

$$\mathrm{C_6H_5Tl[OOCCH(CH_3)_2]_2} + 2\mathrm{HCl} \rightarrow \mathrm{C_6H_5TlCl_2} + 2\mathrm{(CH_3)_2CH\cdot COOH} \tag{5}$$

or

$$n\text{-}\mathrm{BrC_6H_4Tl[OOCCH(CH_3)_2]_2} \xrightarrow{\mathrm{NH_4OH}} n\text{-}\mathrm{BrC_6H_4TlO} \xrightarrow{\mathrm{HCl}} n\text{-}\mathrm{BrC_6H_4TlCl_2}$$

under the experimental conditions likewise does not lead to the appearance of color; consequently, the coloration described in the literature (^{2}) is the result of impurities and is not a property of the substance itself.

Experimental Part

Thallium triisobutyrate (1 mol.) and diphenylmercury (1 mol.). Solutions of 4.65 g of thallium triisobutyrate and 3.6 g of diphenylmercury (each substance in 7 ml of heated dry chloroform) are mixed and left to stand for half an hour at room temperature. The precipitate that separates is filtered off with suction and washed with petroleum ether. 4 g of substance were obtained (87.9%, equation (1)); after recrystallization from dichloroethane it had m.p. 221–222°.

Found %: Tl* 44.82; 44.93
$C_{14}H_{19}TlO_4$. Calculated %: Tl 44.84

Phenylthallium diisobutyrate—white crystals, stable (in contrast to the starting triisobutyrate) in air.

Thallium triisobutyrate (1 mol.) and diphenylmercury (2 mol.). 4.65 g of thallium triisobutyrate, dissolved with heating in 7 ml of dry chloroform, are mixed with 7.1 g of diphenylmercury in 12 ml of the same heated solvent. The mixture is left for half an hour at room temperature. The precipitate that separates is filtered off with suction and washed with petroleum ether. 3.6 g of substance were obtained (80.9% of theory, equation (2)); after recrystallization from dichloroethane it had m.p. 241°.

Found %: Tl 45.59; 45.76
$C_{16}H_{17}TlO_2$. Calculated %: Tl 45.84

Diphenylthallium isobutyrate—white crystalline substance, stable in air.

Thallation of benzene. After heating for 18 h 2.35 g of thallium triisobutyrate with 2.5 ml of dry, thiophene-free benzene (excess) on a boiling water bath in a sealed vessel, and subsequent cooling, the precipitate that separated was filtered off with suction and washed with petroleum ether. The yield of phenylthallium diisobutyrate was 90%. M.p. after recrystallization from dichloroethane, 221°.

Found %: Tl 44.53; 44.41
$C_{14}H_{19}TlO_4$. Calculated %: Tl 44.84

Mixed melting point (see preceding experiment) without depression.

Thallium triisobutyrate and diphenylthallium isobutyrate. 2.25 g (1 mol.) of diphenylthallium isobutyrate (see above) in 45 ml

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* In all cases thallium was determined by the chromate method.

dry chloroform was mixed with 2.35 g (1 mole) of thallium triisobutyrate in 6 ml of the same solvent. After standing overnight in an open flask for partial evaporation of the solvent, the precipitate that had separated was filtered off by suction and washed with petroleum ether. 3.5 g of substance was isolated (an additional 0.9 g from the mother liquor). After recrystallization from dichloroethane, m.p. 221-222°. The m.p. of phenylthallium isobutyrate obtained by the two other methods found by us (see above) is 221°. The yield is practically quantitative.

Mixed sample (see the preceding experiment) without depression.

Conversion of phenylthallium diisobutyrate into phenylthallium dichloride. 2 g of phenylthallium diisobutyrate in 25 ml of methanol was treated with an excess of a 10-15% aqueous ammonia solution. The precipitate that formed was filtered off by suction and washed with water. To its suspension in 20 ml of methanol, a 1.5 *N* solution of hydrogen chloride in the same solvent was added until the reaction to Congo red was acidic. 1.06 g of phenylthallium dichloride was obtained as a white crystalline substance with m.p. 233° (with decomposition). According to the literature data (^{1}), m.p. 235° (with decomposition).

Thallium triisobutyrate (1 mole) and di-*n*-bromophenylmercury (1 mole). To 4.65 g of thallium triisobutyrate dissolved in 7 ml of hot dry chloroform was added a suspension of 5.12 g of di-*n*-bromophenylmercury in 20 ml of the same solvent. At the beginning of mixing, the di-*n*-bromophenylmercury passed into solution, then ceased to dissolve. After the addition of the entire quantity, the mixture was heated until the precipitate dissolved and then cooled to room temperature. The precipitate that separated was filtered off by suction and washed with petroleum ether. Yield 3.2 g (50% of theory; equation (3)). After recrystallization from dichloroethane, the substance melted at 219° (with decomposition, rapid heating).

$C_{14}H_{18}TlBrO_4$.	Found %:	Tl 37.92; 37.77;
	Calculated %:	Tl 38.20

Diisobutyrate of *n*-bromophenylthallium is a white crystalline substance, stable in air.

Conversion of diisobutyrate of *n*-bromophenylthallium into *n*-bromophenylthallium dichloride. To 2.5 g of diisobutyrate of *n*-bromophenylthallium dissolved in 50 ml of alcohol was added an alcoholic solution (1.5 *N*) of hydrogen chloride until an acidic reaction to Congo red appeared. The solution was filtered from turbidity, evaporated at room temperature to a small volume, and the precipitate was filtered off by suction. 1.6 g of substance with m.p. 261° was obtained. After recrystallization from ethyl acetate, m.p. 262°. The m.p. of di-*n*-bromophenylthallium dichloride, according to the literature data (^{6}), is 262-263°.

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Note: Figure translations are in progress. See original paper for figures.