Brief Communications

Organothallium compounds. Reaction of phenylhydrazine with thallium(III) oxide

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Phenylhydrazine reacts with thallium(III) oxide in benzene to give organothallium compounds. Reactions of these compounds with acids afford diphenylthallium salts.

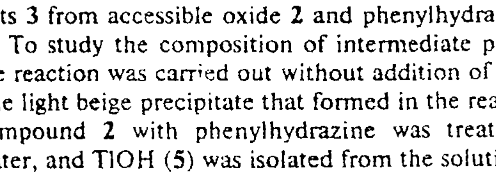
Key words: organothallium compounds, phenylhydrazine, thallium(III) oxide.

Organic derivatives of Tl^{III} (**1**) are normally obtained starting from TlX_3.[1,2] However, anhydrous salts of trivalent thallium are strongly hygroscopic and are readily hydrolyzed; on prolonged storage, they decompose. The synthesis of compounds **1** from organolithium and organomagnesium compounds is accompanied by partial reduction of Tl^{III} salts to Tl^{I} salts.

Previously,[3] we proposed a method for preparation of Alk_2TlX from TlX, Li, and AlkX. The necessity to prepare Ph_2TlX from more accessible and stable thallium derivatives prompted us to use Tl_2O_3 (**2**) in the present study and to carry out its reaction with phenylhydrazine.

Phenylhydrazine easily reacts with oxide **2** in benzene to give intermediate organothallium derivatives. The subsequent treatment of products **1** with acids (HX) leads to the target salts Ph_2TlX (**3**); salts of monovalent thallium (**4**) are formed as side products.

In the case of acetic and trifluoroacetic acids, salts **3** and **4** can easily be separated by washing with water, and in the case of HCl, they are separated by washing with DMF.



$$\underset{\mathbf{2}}{Tl_2O_3} \xrightarrow[2.\ HX]{1.\ PhNH{-}NH_2} \underset{\mathbf{3}}{Ph_2TlX} + \underset{\mathbf{4}}{TlX} + Ph{-}Ph + N_2 + H_2O$$

$X = CF_3COO, CH_3COO, Cl$

This method makes it possible to prepare various salts **3** from accessible oxide **2** and phenylhydrazine.

To study the composition of intermediate products, the reaction was carried out without addition of an acid. The light beige precipitate that formed in the reaction of compound **2** with phenylhydrazine was treated with water, and TlOH (**5**) was isolated from the solution. The insoluble precipitate was found to contain Ph_2TlOH (**6**) and $(Ph_2Tl)_2O$ (**7**). Compound **7** may have been formed from hydroxide **6**, since compound **6** is known to be readily converted into oxide **7** in the presence of an alkali.[4] Thus, the reaction of phenylhydrazine with Tl_2O_3 in benzene yields hydroxides **5** and **6** and oxide **7**.

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Experimental

Benzene was shaken with concentrated H_2SO_4, then washed with a solution of Na_2CO_3 and water, dried with $CaCl_2$, and distilled over sodium. Oxide **2** was obtained by treatment of $Tl(NO_3)_3$ with KOH with heating. The precipitate was filtered off, washed repeatedly with water, and dried *in vacuo* at 100 °C. Phenylhydrazine was distilled *in vacuo*.

Synthesis of diphenylthallium trifluoroacetate. At −20 °C, phenylhydrazine (0.768 g, 7.1 mmol) in 5 mL of benzene was added dropwise under argon over a period of 30 min to a suspension of Tl_2O_3 (**2**) (2.538 g, 5.5 mmol) in 30 mL of benzene stirred with a magnetic stirrer. The color of the dark brown suspension became lighter, and a light beige precipitate was formed. Trifluoroacetic acid (1.31 g, 11.5 mmol) was added to the reaction mixture, and the mixture was stirred for 2 h. The precipitate (3.1 g) was filtered off, washed several times with water, and dried to give 0.48 g (28.6%) of diphenylthallium trifluoroacetate, m.p. 274—276 °C (from ethyl acetate) (*cf.* Ref. 5: m.p. 270—276 °C). Found (%): C, 35.56; H, 2.24; Tl, 43.10. $C_{14}H_{10}F_3O_2Tl$. Calculated (%): C, 35.66; H, 2.14; Tl, 43.34. IR, ν/cm^{-1}: 3062, 3024, 1627, 1570, 1480, 1435, 1196, 1150, 1140, 792.

From the aqueous filtrate, 2.6 g of thallium(I) trifluoroacetate was obtained; m.p. 109—110 °C. The benzene filtrate was analyzed by TLC on Al_2O_3 using a hexane—chloroform (1.5 : 1) mixture as the eluent and I_2 vapor for vizualization. Using a reference compound, it was found that the filtrate contained biphenyl, R_f 0.87. The benzene was evaporated and the biphenyl was isolated and purified by column chromatography on Al_2O_3 using hexane as the eluent. Yield 0.015 g, m.p. 70 °C (*cf.* Ref. 5: m.p. 71 °C).

Diphenylthallium acetate was obtained in a similar way, m.p. 260—262 °C (*cf.* Ref. 5: m.p. 257—261 °C).

Diphenylthallium chloride was obtained by treating intermediate compounds **1** with HCl as described above. The product was extracted from the precipitate with warm DMF and precipitated from the resulting solution by addition of water.

Determination of the composition of intermediate organothallium compounds. Phenylhydrazine (1.043 g, 9.664 mmol) in 6 mL of benzene was added dropwise at room temperature under argon to a suspension of oxide **2** (3.146 g, 6.9 mmol) in 40 mL of benzene stirred with a magnetic stirrer. The reaction mixture was stirred for 2 h, then 80 mL of hot benzene was added, and the mixture was filtered off. This operation was repeated twice to give 3.09 g of a precipitate having alkaline properties. The precipitate was washed several times with water, and the aqueous filtrate was concentrated *in vacuo* under argon to give 1.8 g of hydroxide 5. The residue was washed with warm water. Evaporation of water from the aqueous filtrate *in vacuo* gave 0.2 g of hydroxide **6**, m.p. 221 °C (*cf.* Ref. 6: m.p. 220 °C). Hydroxide **6** was unstable in hot water, and on heating, it was slowly converted into oxide 7. After separation of hydroxide **6**, 0.25 g of water-insoluble oxide 7 was isolated; m.p. 305—308 °C. Found (%): C, 39.27; H, 2.81; Tl, 55.67. $C_{24}H_{20}OTl$. Calculated (%): C, 39.32; H, 2.75; Tl, 55.75.

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