1-PHENYLVINYL COMPOUNDS OF LITHIUM, MERCURY, AND THALLIUM

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In a previous investigation [1] we synthesized various organic compounds of heavy metals. Organo-metallic compounds in which the metal is attached to olefinic carbon, which we have been investigating in recent years, have still received inadequate study [2]. In the present paper we describe more compounds of this type, namely 1-phenylvinyl compounds of mercury and thallium, which were prepared by the action of mercury and thallium salts on 1-phenylvinylthallium. Some metal derivatives of styrene were studied by Nesmeyanov and Kudryavtseva [3].

1-Phenylvinylmercury bromide, m.p. 89.5-90.5°, which was prepared in 33% yield by the action of mercuric bromide on 1-phenylvinylthallium, is readily symmetrized by gaseous ammonia or sodium stannite with formation of bis-1-phenylvinylmercury (m.p. 68-69°). Reaction of this product with mercuric chloride in acetone gave 1-phenylvinylmercury chloride, m.p. 95.5-96°. In ethereal solution 1-phenylvinylthallium reacts smoothly with thallium tribromide with formation of bis-1-phenylvinylthallium bromide (decomposes at 156-158°). With bis-1-phenylvinylmercury thallium tribromide gives bis-1-phenylvinylthallium bromide in 67% yield, and thallium trichloride gives bis-1-phenylvinylthallium chloride (decomposes at 158-160°) in 70% yield. Like diisopropenylthallium bromide, bis-1-phenylvinylthallium bromide reacts with mercury in acetone with formation of bis-1-phenylvinylmercury in 66% yield.

Unlike isopropenyltin compounds [1], 1-phenylvinyltin compounds could not be obtained by reaction between bis-1-phenylvinylmercury and a stannous halide in acetone, benzene, or petroleum ether solution; neither could they be obtained by reaction between bis-1-phenylvinylthallium bromide and stannous bromide or chloride.

EXPERIMENTAL

Ethereal Solution of 1-Phenylvinylthallium. This was prepared in a three-necked flask in an atmosphere of nitrogen from 0.76 g (0.054 mole) of lithium in 140 ml of dry ether and 10 g (0.054 mole) of α-bromo-styrene (b.p. 66° [6 mm], nD 1.5870) in 25 ml of ether. The bromostyrene was added at 8-10° over a period of 90 minutes.

1-Phenylvinylmercury Bromide. Over a period of 30 minutes at 8-10°, 16 g (0.044 mole) of mercuric bromide was added slowly to the ethereal solution of 1-phenylvinylthallium obtained, as described above. The reaction mixture was warmed. After being stirred for one hour, the mixture was decomposed with 1% hydrobromic acid. The ethereal solution was washed with water and dried. Ether was evaporated at the water pump, and the residue was repeatedly recrystallized from acetone. The product, amounting to 7 g (33%), consisted of needles, m.p. 89.5-90.5°.

Found %: C 24.92, 24.93; H 1.89, 1.90. C₈H₆HgBr.

Calculated %: C 25.04; H 1.84.

1-Phenylvinylmercury bromide is readily soluble hot in acetone, chloroform, and benzene, less readily soluble in methanol and ethanol, and sparingly soluble in petroleum ether and carbon tetrachloride.

Symmetrization of 1-Phenylvinylmercury Bromide. A. A solution of 7.9 g (0.02 mole) of 1-phenylvinylmercury bromide in 65 ml of benzene was treated with dry ammonia for 90 minutes. The residue was filtered off, and benzene was evaporated from the filtrate at the water pump. Recrystallization of the residue...
from 3:1 methanol-acetone gave 3.4 g (82%) of crystals, m.p. 68-69°. Further recrystallization did not affect the melting point.

\[
\text{Found } \%: \ C 47.47, 46.89; \ H 3.52, 3.36, \text{ C}_{16}H_{14}Hg. \\
\text{Calculated } \%: \ C 47.23; \ H 3.47.
\]

Bis-1-phenylvinylmercury is soluble in benzene, acetone, and petroleum ether; it is sparingly soluble in methanol and ethanol.

B. Water (10 ml) and alkaline sodium stannate prepared from 0.65 g (0.0028 mole) of SnCl\(_2 \cdot 2H_2O\), 0.5 g of NaOH, and 12 ml of water were added to a solution of 2 g (0.0052 mole) of 1-phenylvinylmercury bromide in 5 ml of acetone. After one hour the precipitate was filtered off, washed with water, dried, and crystallized from petroleum ether. The crystalline product, which amounted to 0.89 g (84%), had a melting point, and also a mixture melting point, of 68.5-69°.

1-Phenylvinylmercury Chloride. Reaction between 1 g (0.0024 mole) of bis-1-phenylvinylmercury in 2 ml of acetone and 0.66 g (0.0024 mole) of mercuric chloride gave 1.44 g (86%) of leaflets, m.p. 95-96°.

\[
\text{Found } \%: \ C 28.22, 28.23; \ H 2.16, 2.03, \text{ C}_{16}H_{14}HgCl. \\
\text{Calculated } \%: \ C 28.33; \ H 2.08.
\]

1-Phenylvinylmercury chloride is readily soluble hot in acetone, methanol, and ethanol; it is sparingly soluble in petroleum ether.

Bis-1-phenylvinylthallium Bromide. A. A solution of 8 g (0.018 mole) of thallium tribromide in 35 ml of ether was added to the ethereal solution of 1-phenylvinylthallium. The mixture was stirred for 30 minutes and then decomposed with 1% hydrobromic acid. After being washed and dried, the precipitate weighed 4.94 g. Recrystallization from acetone gave 3.01 g (22%) of needles, which decomposed without melting at 156-158°. This substance is soluble in pyridine, sparingly soluble in acetone, very sparingly soluble in methanol and ethanol, and insoluble in petroleum ether.

\[
\text{Found } \%: \ C 39.23, 39.29; \ H 3.01, 3.00; \text{ Br 16.25, 16.39, C}_{16}H_{14}TIBr. \\
\text{Calculated } \%: \ C 39.17; \ H 2.88; \text{ Br 16.29.}
\]

B. A solution of 0.82 g (0.0018 mole) of thallium tribromide in 3.5 ml of ether was added to 1.5 g (0.0037 mole) of bis-1-phenylvinylmercury in 3 ml of ether. After one hour the precipitate was filtered off and washed repeatedly with cold acetone. Recrystallization from acetone gave 0.61 g (67%) of bis-1-phenylvinylthallium bromide, which decomposed at 156-158°.

\[
\text{Found } \%: \ C 39.31, 39.30; \ H 2.95, 2.98; \text{ Br 16.45, 16.48, C}_{16}H_{14}TIBr. \\
\text{Calculated } \%: \ C 39.17; \ H 2.88; \text{ Br 16.29.}
\]

Some of the solvent was evaporated from the main filtrate, and 1.11 g (73%) of 1-phenylvinylmercury bromide was isolated; its melting point, and also its mixture melting points, was 89-90.5°.

Bis-1-phenylvinylthallium Chloride. Reaction between 1.5 g (0.0037 mole) of bis-1-phenylvinylmercury and 0.55 g (0.0017 mole) of thallium trichloride under conditions similar to those of the reaction with thallium tribromide gave 0.58 g (70%) of fine needles which decomposed at 158-160°.

\[
\text{Found } \%: \ C 42.85, 43.10; \ H 3.21, 3.16; \text{ Cl 7.75, 8.03, C}_{16}H_{14}TICl. \\
\text{Calculated } \%: \ C 43.07; \ H 3.16; \text{ Cl 7.95}
\]

Bis-1-phenylvinylthallium chloride is readily soluble in pyridine, sparingly soluble in acetone, methanol, and ethanol, and insoluble in petroleum ether. The filtrate yielded 0.95 g (76%) of 1-phenylvinylmercury chloride, m.p. 95-96°.

Reaction between Bis-1-phenylvinylthallium Bromide and Mercury. A mixture of 1.0 g (0.002 mole) of bis-1-phenylvinylthallium bromide, 10 g of mercury, and 25 ml of acetone was stirred for five hours at 40°. The clear solution was decanted, solvent was evaporated, and the residue was recrystallized from 1:3 methan-