[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, THE HEBREW UNIVERSITY]

Mercury Derivatives of 1,1-Diphenylethane and 1,1-Diphenylethylene

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1,1-Diphenylethylene (I) and mercuric acetate react smoothly both in aqueous and methanolic solution, giving the corresponding addition products of hydroxy- and methoxymercuric acetate, respectively (II, VII). Dehydration of II or the chloride IV yields the corresponding diphenylvinylmercury compounds V and VI.

2,2-Diphenyl-2-hydroxyethylmercuric Acetate (II).—A mixture of 36 g. of I and a solution of 64 g. of mercuric acetate in 200 ml. of water was stirred for five hours. A sticky precipitate was formed, which was broken up several times during the reaction. The next day it was collected, washed with water and dried. Recrystallized from ethanol, colorless needles were obtained; m. p. 123°.

Anal. Calcd. for $C_{16}H_{16}O_3Hg$: C, 42.1; H, 3.5. Found: C, 42.6; H, 4.0.

Recrystallized from benzene, slender, colorless prisms were obtained, which contained 0.5 mole of benzene. When heated slowly, they melted at 123°, after strong preliminary sintering; upon quick heating they melted at 110–112°, resolidified and melted finally at 123°. The benzene is retained *in vacuo* at 60°, but is given off at 110°; yield 58 g. (58.5%).

Anal. Calcd. for $C_{16}H_{16}O_3Hg \cdot 0.5C_6H_6$: C, 46.0; H, 3.8; volatile, 7.9. Found: C, 46.4; H, 3.8; volatile, 8.0.

The corresponding iodide III was obtained from II with potassium iodide in acetone, in 94% yield; m. p. 118° (from benzene).

Anal. Calcd. for $C_{14}H_{13}OIHg$: C, 32.1; H, 2.5. Found: C, 32.1; H, 2.7.

The chloride IV was prepared from II in acetone–ethanol, with saturated aqueous sodium chloride solution in 95% yield, m. p. 148°.

Anal. Calcd. for $C_{14}H_{13}OClHg$: C, 38.8; H, 3.0. Found: C, 39.2; H, 3.1.

(2,2-Diphenylvinyl)-mercuric Acetate (V).—Ten grams of II and 25 ml. of acetic anhydride were heated on the water-bath for one hour. The mixture was diluted with water. The resulting precipitate, crystallized from ethanol, gave long colorless needles, melting at 130°. The yield varied from 30 to 60%.

Anal. Calcd. for $C_{16}H_{14}O_2Hg$: C, 43.8; H, 3.2. Found: C, 43.5; H, 2.9.

Treatment with sodium chloride gave in 90% yield the corresponding chloride VI. It crystallized in platelets from benzene; m. p. 142–143°. The same substance was also obtained by dehydration of IV, but in very small yields.

Anal. Calcd. for $C_{14}H_{11}ClHg$: C, 40.5; H, 2.7. Found: C, 40.6; H, 2.8.

2,2-Diphenyl-2-methoxyethylmercuric Acetate (VII).—A mixture of 32 g. of mercuric acetate, 200 ml. of methanol and 18 g. of I was shaken for fifteen minutes, then 160 ml. of the methanol was distilled off and 100 ml. of water was added. The white precipitate was filtered and crystallized from methanol; m. p. 107°, yield 23 g. (49%).

Anal. Calcd. for $C_{17}H_{18}O_3Hg$: C, 43.3; H, 3.8. Found: C, 43.1; H, 3.8.

The corresponding chloride VIII was obtained in 97% yield from VII and sodium chloride; m. p. 177° (from benzene).

Anal. Calcd. for $C_{15}H_{15}OClHg$: C, 40.3; H, 3.4. Found: C, 40.6; H, 3.3.

In some preliminary experiments we found that I, on heating with arsenious chloride alone, underwent dimerization, giving 1,1,3,3-tetraphenyl-1-butene (IX),[1,2] while in the presence of mercuric chloride, 1,1,3-triphenyl-3-methylindane (X)[1,2,3] was obtained. After preparing the above mercury compounds, we tried to substitute the –HgX group by the –$AsCl_2$ group,[4] but did not succeed in isolating any arseno compound, the only product obtained being X.

Arsenious chloride (5 ml.) and 1.5 g. of I, heated at 100° for four hours, gave 80% of IX, identified by melting point (112–113°) and mixed melting point with an authentic sample. The same substances in the presence of mercuric chloride (1.5 g.), as well as arsenious chloride and II, III, V, VI and VIII gave near quantitative yields of X. This was identified by melting point (142°), mixed m. p. with authentic samples and also by analysis.

Arsenious chloride on contact with I or its mercury derivatives gave for a few seconds a brown or red color, which changed immediately to a deep, brilliant green.

It seems, that the presence of mercury salts, either as such, or contained in the reacting molecule and possibly splitting off in one of the first steps of the reaction, parallels the action of dry hydrochloric acid in the dimerization of I by stannic chloride.[2] The formation of X from I could be explained on the same general lines as the dimerization of styrene to 1-phenyl-3-methylindane.[5] The same could be applied for the formation of X from II, III and VIII, supposing as one of the steps of the reaction the elimination of basic (or methoxy-) mercuric salts. The only explanation we can propose for the formation of X from V and VI is that the reaction mixture (although protected by a $CaCl_2$ tube), or the arsenious chloride before the reaction, absorbed enough moisture to account for the gain of two hydrogen atoms in the dimer formed, via the reaction $AsCl_3 + H_2O \rightarrow HCl$; $Ph_2C{=}CHHgX + HCl \rightarrow Ph_2C{=}CH_2 + HgXCl$.

Summary

Several new mercury compounds of 1,1-diphenylethylene were prepared. The reaction of these compounds with arsenious chloride was investigated and the product identified as 1,1,3-triphenyl-3-methylindane.

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(3) Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

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(5) Williams and Thomas, *J. Chem. Soc.*, 1867 (1948).