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Abstract

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Synthesis of Ethylmercury Salts

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Ethylmercury salts C_2H_5HgX (where $X = Cl, PO_4$, etc.) are used as valuable fungicides. The industrial method for obtaining ethylmercury salts is based on the reaction between HgX_2 and diethylmercury, which, in turn, is obtained from low-percentage sodium amalgam and ethyl bromide ([1–4]). In addition, compounds C_2H_5HgX can be synthesized via organomagnesium compounds ([1]), and also by the action of tetraethyllead on mercury phosphate ([5]), etc. ([2]).

Our method for obtaining ethylmercury salts is based on the decarboxylation of mercury propionate under the action of peroxides or ultraviolet light

$$C_2H_5COOHgOCOC_2H_5 \xrightarrow[\text{or light}]{\text{peroxide}} C_2H_5HgOCOC_2H_5 + CO_2.$$

The anion of ethylmercury propionate can readily be replaced by any other anion.

The highest yields of ethylmercury propionate (88.8%) were obtained by us in the reaction of mercury propionate with propionyl peroxide in propionic acid at 97–98°. The reaction was carried out as follows. To a heated solution of 10.4 g (0.03 mole) of mercury propionate in 100 ml of propionic acid, a solution of 8.75 g (0.06 mole) of propionyl peroxide in 40 ml of propionic acid* was added over the course of 2 hr. After addition of all the peroxide, heating and stirring were continued for another 1.5 hr. After completion of the reaction, propionic acid was distilled off from the reaction mass under reduced pressure; the residue was dissolved in water, and, by the action of potassium chloride on the solution, ethylmercury chloride was obtained. Weight 4.89 g, m.p. 194°, yield 61.5%. By treating the mother liquor with potassium iodide, an additional 2.92 g of ethylmercury iodide was isolated; m.p. 181°, yield 27.3%. The total yield of ethylmercury salts was 88.8%.

The propionyl peroxide required for the reaction can be obtained directly in the reaction mass. To a mixture of 10.4 g of mercury propionate (0.03 mole), 100 ml of propionic acid, and 40 ml of propionic anhydride, 10 ml of 42% hydrogen peroxide was added at room temperature over the course of 20 min with stirring. The mixture was stirred at room temperature for another 25 min, and then heated on a boiling water bath. Heating and stirring were continued for 2 hr,

after which 5.57 g of ethylmercury chloride (70.0%) and 0.68 g of ethylmercury iodide (6.35%) were isolated from the reaction mass by the method described above. Thus, the total yield of ethylmercury salts was 76.3% of theory.

Decarboxylation of mercury propionate also proceeds under the action of ultraviolet light. 10.4 g of mercury propionate in 150 ml of boiling propionic acid was irradiated for 80 min with a mercury–quartz lamp

* The propionic-acid solution of propionyl peroxide was prepared by adding, over the course of 1 hr, 10 ml of 27% hydrogen peroxide to a mixture of 52 g of propionic anhydride and 2 g of solid sodium hydroxide, with cooling by snow and water and vigorous stirring.

PRK-4 in the apparatus described earlier ([6]). The ethylmercury salts were isolated by the method described above. 7.27 g of ethylmercury iodide was obtained. Yield 68.0% of theory.

It should be noted that the yields of ethylmercury compounds in the photochemical reaction depend strongly on the duration of irradiation, since with insufficient irradiation not all the salt has time to react; with more prolonged irradiation, however, the ethylmercury propionate that has formed undergoes further decomposition to metallic mercury. The method for obtaining ethylmercury salts from mercury propionate and propionyl peroxide is free from this drawback. Decomposition of mercury propionate can also be induced by other peroxides, for example benzoyl peroxide. However, this leads to a decrease in the yield of ethylmercury compounds and to their contamination with phenylmercury salts.

Thus, decarboxylation of mercuric propionate is most conveniently carried out under the action of propionyl peroxide (which can be obtained directly in the reaction mixture). This method makes it possible to obtain ethylmercury salts in high yields.

Work on the preparation of alkylmercury compounds is continuing.

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