

obtained was reddish-brown, insoluble in organic solvents, and did not melt under 250°; yield, 45%.

Anal. Subs., 0.1585, 0.2067: 9.35 cc., 12.20 cc. of 0.0957 *N* iodine soln. Calcd. for $C_{24}H_{24}O_4N_2As_2$: As, 22.25. Found: 21.71, 21.72.

Summary

By the condensation of isatin or substituted isatins with arsono-acetophenones, arsonophenyl-cinchoninic acids have been prepared. The corresponding esters and arsono derivatives are easily produced. All of these substances proved to be much more toxic than arsphenamine or arsanilic acid and not as trypanocidal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, No. 29]

MERCURY DERIVATIVES OF SOME IMIDES

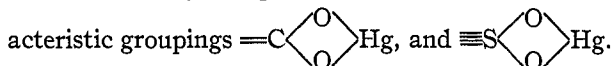
BY EDWARD LYONS

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Amides and imides yield mercury derivatives in which the mercury is attached to nitrogen. Succinimide¹ gives the compound $(CH_2CO)_2N-Hg-N(CH_2CO)_2$; phthalimide^{1c} similarly gives $C_6H_4(CO)_2N-Hg-N(CO)_2C_6H_4$. Saccharin² has been reported to yield compounds that are either insoluble, or soluble only in physiological salt solution.

The present paper describes the preparation and properties of a new class of mercury compounds, obtained from imides, containing the characteristic groupings

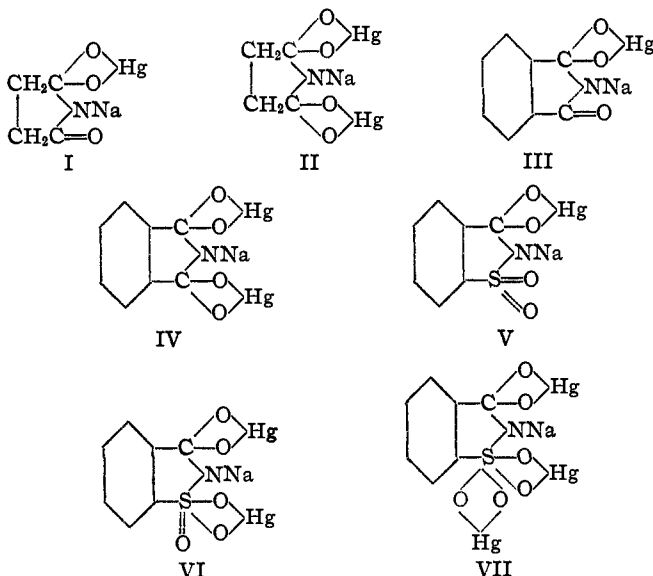


New Mercury Compounds of Imides

When imides such as succinimide, phthalimide or saccharin react in alkaline solution with freshly prepared mercuric oxide, or better, with mercuric salts and an excess of base, there are formed alkali salts of substances containing mercury linked to $=C=O$ or $\equiv S=O$ groups. The number of mercury atoms which can be introduced is limited to the number of these doubly-linked oxygen atoms. Thus, succinimide gives a mono- and dimercury compound (I and II). Phthalimide presents similar possibilities (III and IV). Saccharin gives three compounds, which may be represented by V, VI and VII.

¹ (a) Dessaignes, *Ann.*, **82**, 234 (1852). (b) Menschutkin, *Ann.*, **162**, 171 (1871). (c) Landsberg, *Ann.*, **215**, 209 (1883).

² Dufournel, *Bull. soc. chim.*, [3] **25**, 326 (1901). Auld, *J. Chem. Soc.*, **91**, 1048, (1907). Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., 1921, p. 309.



The sodium salts obtained are either neutral or slightly alkaline. Treatment with cold dil. acids yields the corresponding hydrogen compounds. Hot concd. acids and bases decompose the compounds. Hydrogen sulfide precipitates mercuric sulfide at once. The attachment of the mercury is more stable than in the common O-Hg and N-Hg compounds, but is not as stable as in the true organic compounds of mercury.

Mercury Compounds of Succinimide

The well-known mercury succinimide used in syphilis therapy is $(C_4H_4O_2N)_2Hg$, with a mercury content of 50.5%, made by the action of mercuric oxide on an aqueous solution of succinimide.¹ The mercury in this compound behaves towards reagents like inorganic mercury. The new mercury derivatives of succinimide may be obtained as follows.

Monomercury Derivative.—To an ice-cold solution of 2.97 g. (1 molecular equivalent) of succinimide in 30 cc. of water containing about 5.6 g. of potassium hydroxide is added, in portions, a solution of 9.5 g. of mercuric acetate in about 20 cc. of water. The solution is then filtered and the filtrate, when poured into alcohol, yields a yellow powder. This is very soluble in water. The solution is golden-yellow and alkaline to phenolphthalein. Strong acids decompose it. Heating it with concd. sodium hydroxide also causes decomposition with liberation of ammonia. The substance varies somewhat in mercury content (55–58%) depending on the degree of purity. A compound corresponding to the formula $C_4H_4O_2NHgK$ should have a mercury content of 56.67%.

Dimercury Derivative.—The starting material for this compound is the monomercury derivative. To 3.53 g. (1 molecular equivalent) of the mono compound in 15 cc. of water is added 1.12 g. (2 equivalents) of potassium hydroxide followed by a cold solution of 3.18 g. (1 equivalent) of mercuric acetate in 15 cc. of water. The greenish-colored solution obtained yields, from alcohol, a greenish-yellow, water-soluble

powder. This substance, as well as the mono derivative, is fairly stable when dry but when moist both decompose with the formation of mercuric oxide.

Anal. Calcd. for $C_6H_4O_4NHg_2K$: Hg, 70.3. Found: 70.12.

The successful preparation of the mono derivative is not always easy. Very frequently an insoluble substance is formed. This is filtered off and the filtrate is then precipitated by pouring into alcohol. The yield, however, is considerably decreased.

Mercury Compounds of Phthalimide

When sodium phthalimide in solution is treated with a solution of a mercuric salt, a white precipitate having the composition, $(C_8H_4O_2N)_2Hg$, (Hg = 40.65%) is obtained.^{1c}

The preparation of the new compound is as follows.

Monomercury Derivative.—To 1.47 g. (1 molecular equivalent) of phthalimide dissolved in a warm solution of 1.29 g. (3 equivalents) of sodium hydroxide in 7.5 cc. of water is added 3.18 g. (1 equivalent) of mercuric acetate in 15 cc. of water, drop by drop. A clear solution is obtained. Upon precipitation with alcohol a white, water-soluble powder is obtained.

Anal. Calcd. for $C_8H_4O_2NHgNa$: Hg, 51.8. Found: 51.21.

Dimercury Derivative.—To the warmed solution of 3.86 g. (1 molecular equivalent) of the monomercury derivative in 10 cc. of solution containing 0.8 g. of sodium hydroxide is added, drop by drop, a solution of 3.18 g. (1 equivalent) of mercuric acetate in 15 cc. of water. An orange-colored solution is obtained. Poured into alcohol it gives a yellow precipitate that turns slightly darker on drying.

Anal. Calcd. for $C_8H_4O_4NHg_2Na$: Hg, 66.6. Found: 66.27.

Like the derivatives of succinimide, these compounds are not easily obtained pure. They are more stable than the former and their solutions may be boiled without decomposition. Cold, dil. acids precipitate the acid compound. Hot acids and alkalis decompose them.

New Mercury Compounds of Saccharin

Monomercury Derivative.—A solution of 1.83 g. (1 molecular equivalent) of saccharin is made in 6.0 cc. of boiling solution containing 1.2 g. (3 equivalents) of sodium hydroxide. To this is added, in portions, a hot solution of 3.18 g. (1 equivalent) of mercuric acetate in 15 cc. of water. Should the final portion give a precipitate that does not dissolve readily, a small amount of saccharin and a few drops of sodium hydroxide are added. The solution is almost colorless. It is filtered into alcohol. A white or slightly yellow powder is obtained. The salt is very soluble in water. Its solution is either neutral or only faintly alkaline. Dil. acids precipitate the acid substance.

Anal. Calcd. for $C_7H_4O_4NSHgNa$: Hg, 47.5. Found: 47.35.

Dimercury Derivative.—Although the dimercury compound can be made directly, the resulting product is not pure. Better results are obtained by using the mono derivative as the starting substance. To 4.21 g. (1 molecular equivalent) of mono-derivative in 75 cc. of boiling water is added 0.8 g. (2 equivalents) of sodium hydroxide in solution, and then a hot solution of 3.18 g. (1 equivalent) of mercuric acetate in 15 cc. of water. Should some of the precipitate formed fail to redissolve, a few drops of sodium hydroxide are added. The solution is filtered into alcohol. A practically white powder is obtained. It corresponds in its general properties to the mono derivative.

Anal. Calcd. for $C_7H_4O_6NSHg_2Na$: Hg, 62.8. Found: 63.1.

Trimercury Derivative.—A solution of 6.37 g. (1 molecular equivalent) of the dimercury compound in 15 cc. of warm water is treated with a hot solution containing 0.8 g. (2 equivalents) of sodium hydroxide, and then with a boiling solution of 3.18 g. (1 equivalent) of mercuric acetate in 15 cc. of water. The resulting greenish-colored solution when poured into alcohol gives a greenish-yellow powder. It dissolves in water giving a solution with a slightly alkaline reaction.

Anal. Calcd. for $C_7H_4O_6NSHg_3Na$: Hg, 70.3. Found: 70.5.

The stability of these substances varies with the number of mercury atoms present. The mono derivative is the most stable. All are very soluble in water and are decomposed at once by hydrogen sulfide. Dil. acids precipitate the acid substance. Concd. acids and boiling alkalis react drastically. Attempts to introduce a fourth mercury atom invariably failed. In several cases, green products, not very soluble and having a mercury content of about 73%, were obtained.

Summary

New mercury compounds of succinimide, phthalimide and saccharin have been prepared and described. The linkage of the mercury is of a new type, intermediate in stability between that in ordinary mercury salts of oxygen acids and organic mercury compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, No. 464]

THE THERMOLABILITY OF COLLAGEN¹

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The discovery of the second point of minimum swelling of gelatin at *PH* 7.7 by Wilson and Kern,² and a corresponding second point of minimum swelling of calfskin at *PH* 7.6 by Wilson and Gallun³ has aroused new interest in the chemical behavior of these proteins in solutions on the alkaline side of *PH* 4.7 or 5.0, the accepted iso-electric points.

The absorption spectrum of gelatin measured at different hydrogen-ion concentrations by Higley and Mathews⁴ likewise shows two points of minimum: the first at *PH* 4.69, corresponding with the "first iso-electric point," and the second at *PH* 7.65, corresponding with the "second iso-electric point."

In extended studies of the rate of fixation of vegetable tannins by hide substance at room temperature as a function of the hydrogen-ion concentra-

¹ Presented before the Division of Leather Chemistry at the 66th meeting of the American Chemical Society, Milwaukee, Wis., September 10-14, 1923.

² Wilson and Kern, *THIS JOURNAL*, **44**, 2633 (1922).

³ Wilson and Gallun, *Ind. Eng. Chem.*, **15**, 71 (1923).

⁴ Higley and Mathews, *THIS JOURNAL*, **46**, 852 (1924).