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THE MERCURATION OF AURIN AND ATTEMPTS TO MERCURATE SOME OTHER TRIPHENYLMETHANE DYES

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The original purpose of this study was to make organic mercury derivatives of crystal violet with the hope that they might be valuable therapeutically. This aim was not achieved. While dimethylaniline and similar substances are mercurated with the greatest ease, less basic amino compounds are not.[1]

No successful mercuration was obtained with crystal violet, N-phenyl methyl violet or malachite green. A small amount of a dimercurated product was obtained from the base of malachite green. It was too insoluble for further study. On the other hand, pararosaniline was mercurated with relative ease. The product was the acetate of triacetoxymercuri-pararosaniline. It was so insoluble that it could not be changed to the corresponding chloromercuri compound.

It was next decided to mercurate aurin. This process proved to be unusually easy, as was to be expected from the work of Wolvekamp on the corresponding tricarboxylic acid.[2] In the present study modified methods of mercuration were developed which made it possible to obtain products containing one, two or three atoms of mercury by merely modifying the solvent. In a mixture of ethyl acetate and acetic acid the monomercury product was obtained. In alcohol solution the chief product was the very insoluble tri-mercury compound. By using a mixture of alcohol and acetic acid and a relative excess of aurin, the di-mercury product was obtained. When the mono-acetoxymercuri-aurin was refluxed alone in alcohol, it was converted to the triacetoxymercuri compound and free aurin.

The explanation of these reactions is that the mercuration reactions are reversible. The use of alcohol removes the acetic acid formed in the mercuration reaction and favors the formation of the very insoluble trimercury product. An increase in the acetic acid concentration favors the di-mercury product. With ethyl acetate and acetic acid and no alcohol, the mercuration is made most difficult and only the mono-mercury compound is obtained. Further evidence for this conception is given by the conversion of acetoxymercuri-aurin to the tri-mercury compound by heating in alcohol and to the trichloromercuri-aurin by heating with sodium chloride solution.

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[1] Kharasch and Jacobsohn, THIS JOURNAL, **43,** 1894 (1921); Chalkley, *ibid.*, **47,** 2055 (1925).

[2] Wolvekamp, U. S. Patent 1,412,440; *C. A.*, **16,** 2199 (1922).

All of the organic mercury compounds obtained in this study were split by sodium iodide to give inorganic mercury and sodium hydroxide.[3]

Experimental

Mercuration of Pararosaniline.—A solution of 5 g. (0.014 mole) of pararosaniline acetate and 2 g. (0.006 mole) of mercuric acetate in 500 cc. of water containing 1 cc. of acetic acid was refluxed for three hours. The solution then gave no test for inorganic mercury. After addition of 3 g. (0.009 mole) more mercuric acetate the mixture was refluxed for five hours longer. Inorganic mercury was then present. After three more hours of refluxing only organic mercury was present. On cooling the whole mixture set to a thin jelly. This was evaporated to a volume of 200 cc. It was then filtered by suction, a process requiring several days. The residue was dried first at 50° and then at 80°. It was extracted repeatedly with 95% alcohol and dried again. The product was triacetoxymercuripararosaniline acetate.

Anal. Calcd. for $C_{27}H_{27}O_8N_3Hg_3$: Hg, 53.6. Found: Hg, 52.6, 52.5.

It is a dark brown solid very sparingly soluble in water. After thorough drying it is much more difficultly soluble. It is insoluble in other solvents. When refluxed with an excess of aqueous sodium iodide the mercury is removed quantitatively with the formation of sodium mercuric iodide, sodium hydroxide and pararosaniline base.

The preparation of the mercury compound was repeated according to several other sets of conditions without any noticeable change in the results. The products obtained contained the following percentages of mercury: 52.6, 52.7, 53.1.

Attempts to prepare mercury derivatives of pararosaniline containing one or two atoms of mercury were unsuccessful.

Attempted Mercuration of Malachite Green and its Base.—This substance was treated with mercuric acetate under a great variety of conditions. The solvents used included various concentrations of ethyl alcohol, acetic acid, ethyl acetate, benzene and mixtures of these. The time of heating varied from a few minutes to ten days. In no case was there any evidence of formation of organic mercury compounds. In all cases considerable amounts of mercury and mercurous compounds were formed, indicating oxidation of the dye. In one run in glacial acetic acid a small amount of dimethylaminobenzophenone, m. p. 93–94°, was obtained. In several cases addition products containing inorganic mercury were obtained.

When the mercuration was repeated at a higher temperature by refluxing the free base of malachite green for twenty hours in *n*-butyl acetate, oxidation was the only result, all of the mercury being converted to metal.

Attempted Mercuration of Other Basic Triphenylmethane Dyes.—Similar experiments were carried out with crystal violet (N-hexamethyl pararosaniline), N-phenyl methyl violet (N-phenyl-N-pentamethyl pararosaniline). In no case was an organic mercury compound obtained.

Acetoxymercuri-aurin.—A solution of 4.8 g. (0.16 mole) of aurin and 5.7 g. (0.18 mole) of mercuric acetate in 80 cc. of dry alcohol-free ethyl acetate containing 20 cc. of glacial acetic acid was refluxed with stirring for six hours. No inorganic mercury remained. The precipitate was removed, washed with alcohol and dried.

Anal. Calcd. for $C_{21}H_{16}O_5Hg$: Hg, 36.5. Found: Hg, 35.8, 36.0.

A larger run using 48 g. of aurin, 58 g. of (90%) mercuric acetate, 240 g. of glacial acetic acid and 760 cc. of 90% ethyl acetate gave 83 g. of the acetoxymercuri-aurin (91% of the calculated amount). Analyses gave 36.4 and 36.5% of mercury.

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[3] Whitmore and Middleton, This Journal, **43,** 619 (1921).

If much more than one molecular equivalent of mercuric acetate was used in the above solvent mixture, inorganic mercury remained even after long refluxing.

Acetoxymercuri-aurin is a red powder soluble in alcohol, acetone and alkalies. When refluxed with sodium iodide solution the carbon–mercury linkage is split with the formation of sodium hydroxide.

Diacetoxymercuri-aurin.—A solution of 19.3 g. (0.065 mole) of aurin and 6 g. (0.17 mole) of 90% mercuric acetate in 300 cc. of 95% alcohol and 12 cc. of glacial acetic acid was refluxed for half an hour with stirring. Longer refluxing gave some of the black trimercurated product. Shorter refluxing gave a smaller yield of dimercurated product. The mixture was cooled and filtered. The product was washed with alcohol and dried at 50°. Diacetoxymercuri-aurin is a bright red powder. It is soluble in alcohol, acetone, ethyl acetate and alkalies.

Anal. Calcd. for $C_{23}H_{18}O_7Hg_2$: Hg, 49.7. Found: Hg, 49.9, 49.2, 50.0.

Triacetoxymercuri-aurin.—A solution of 14.5 g. (0.05 mole) of aurin and 32.0 g. (0.1 mole) of mercuric acetate in 300 cc. of 95% alcohol, 50 cc. of water and 15 cc. of acetic acid was refluxed with stirring for fifteen hours. No inorganic mercury remained. The greenish-black precipitate was collected on a filter, washed with alcohol and dried; wt., 22 g. A similar run using mercuric acetate and aurin in the molar ratio of 3:1 gave the same product. Mercury analyses gave 56.2 and 56.4. Triacetoxymercuri-aurin is a black powder somewhat soluble in alcohol, acetic acid and alkalies.

Anal. Calcd. for $C_{25}H_{20}O_9Hg_3$: Hg, 56.5. Found: Hg, 56.9, 56.7.

Conversion of Acetoxymercuri-aurin to Triacetoxymercuri-aurin.—A mixture of 5 g. of acetoxymercuri-aurin in 100 cc. of 95% alcohol was refluxed for 24 hrs. The hot mixture was filtered and the red filtrate discarded. The residue was refluxed with 100 cc. more alcohol for twenty-four hours. It was again filtered, giving a yellow filtrate. The residue was washed with alcohol and dried at 90°, the product being triacetoxymercuri-aurin. It was dark red, whereas the product obtained by direct mercuration was black.

Anal. Calcd. for $C_{25}H_{20}O_9Hg_3$: Hg, 56.5. Found: Hg, 56.9, 56.9.

Trichloromercuri-aurin was prepared from the acetate and sodium chloride in alcohol by refluxing for three days.

Anal. Calcd. for $C_{19}H_{11}O_3Cl_3Hg_3$: Hg, 60.5. Found: Hg, 59.7, 60.5, 60.3.

The same product was obtained by refluxing 5 g. of acetoxymercuri-aurin and 3.5 g. of sodium chloride in 150 cc. of alcohol for three days. It gave mercury analyses of 60.0 and 59.8%.

No way was found of making chloromercuri-aurin.

Summary

1. Pararosaniline yields a triacetoxymercuri compound readily. The base of malachite green gives a small yield of a diacetoxymercuri compound.

2. Aurin gives mono-, di- and triacetoxymercuri compounds depending on the solvent used.

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