

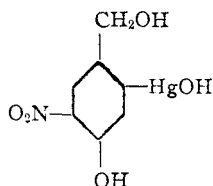
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

### 3-NITRO-4-HYDROXY-5-IODO-BENZOIC ACID AND THE MERCURY DERIVATIVE OF PARA-HYDROXY-META-NITROPHENYL CARBINOL.

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Some time ago<sup>2</sup> Hart and Hirschfelder published a paper on "Mercury Compounds of some Phenyl Carbinols," in which they describe a mercury compound of *p*-hydroxy-*m*-nitrophenyl carbinol. The position of the mercury in that compound is tentatively assumed by the authors to be *meta* to the hydroxyl group, *i. e.*,



Their evidence is confined to the fact that the compound did not lose water, to form an inner anhydride, when heated to 110° for some time.

However, the position of the mercury, *meta* to an hydroxyl group, constituted such a marked disagreement with that taken by mercury in the mercurization of nitrophenols and substituted nitrophenols<sup>3</sup> that the writer decided to investigate more closely the structure of this compound, and obtain direct evidence as to its constitution. The work was also prompted by the fact that the writer had to identify the position of the mercury in the product obtained by heating the mercury salt of 3-nitro-4-hydroxy-benzoic acid, in connection with another investigation, the results of which will appear shortly.

The plan of attack was then as follows: the mercury compound obtained by heating *p*-hydroxy-*m*-nitrophenyl carbinol with mercuric acetate, according to the directions of Hart and Hirschfelder, was treated with the calculated amount of potassium periodide, and the iodo derivative, thus formed, oxidized to the corresponding carboxylic acid, by the use of an excess of potassium permanganate in alkaline solution.

The acid thus obtained was found to agree in properties with that prepared by direct nitration of 3-iodo-4-hydroxy-benzoic acid. This then proves most conclusively that the position of the mercury in the compound prepared by Hart and Hirschfelder is *ortho* to the hydroxyl group and, therefore, quite in agreement with the mercurization of nitro phenols.

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<sup>2</sup> Hart and Hirschfelder, *THIS JOURNAL*, **42**, 2678 (1920).

<sup>3</sup> Hantzsch and Auld, *Ber.*, **39**, 1108 (1906); Raiziss, Kolmer and Gavron, *J. Biol. Chem.*, **40**, 533 (1919); Stieglitz, Kharasch and Hanke, *THIS JOURNAL*, **43**, 1185 (1921).

The 3-nitro-4-hydroxy-5-iodo-benzoic acid herein described has been prepared by Weselsky,<sup>1</sup> by treating 3-nitro-4-hydroxy-benzoic acid with iodine and mercuric oxide. No proof is given, however, that the iodine enters *ortho* to the hydroxyl group. It was for this reason that the acid was prepared by nitrating 3-iodo-4-hydroxy-benzoic acid, and the constitution proved thus by its identity with that obtained from the mercury compound of *p*-hydroxy-*m*-nitrophenyl carbinol, and that from the mercury compound of 3-nitro-4-hydroxy-benzoic acid.

#### Experimental Part.

**Preparation of 3-nitro-4-hydroxy-5-iodo-phenyl carbinol.**—To a suspension of 3.4 g. of the mercury compound of 3-nitro-4-hydroxy-phenyl carbinol, in 75 cc. of water, 21 cc. of a solution of potassium periodide, containing 0.1 g. of iodine per cc., was added, in small portions, and the mixture well shaken. After the color of the iodine disappeared (1.5 hours), the precipitate was collected on a filter, washed well with water, and then treated with sodium carbonate. A small amount of mercuric iodide remained undissolved, and was filtered off. The filtrate was acidified with hydrochloric acid. A yellow precipitate separated which was collected on a filter, and dried *in vacuo*. Yield 1.8 g.

For analysis the compound was crystallized from 20% alcohol, and dried to constant weight *in vacuo* over sulfuric acid.

*Analysis:* Subs., 0.2139: 9.30 cc. dry N<sub>2</sub> at 22° and 729.2 mm. Calc. for C<sub>7</sub>H<sub>6</sub>O<sub>4</sub>NI: N, 4.73. Found: 4.82.

The compound is of a light yellow color. It crystallizes from very dilute alcohol in the form of small yellow needles. It is soluble in hot water and most organic solvents. M. p. 138°.

**The Preparation of 3-nitro-4-hydroxy-5-iodo-benzoic Acid.**—5-Iodo-4-hydroxy-benzoic acid (m. p. 174.5°) was nitrated by dissolving it in a large volume of hot water, and then adding dil. nitric acid. It was found best to boil the solution for 15 minutes. After the solution had cooled, the precipitate which separated was collected on a filter, washed well with water, and dried in the oven at 100°. M. p. 235°. After a single crystallization from dilute alcohol the melting point was 251°. For analysis the compound was dried at 100° *in vacuo*.

*Analysis.* Subs., 0.2567: 10.72 cc. dry N<sub>2</sub> at 22° and 727.2 mm. Calc. for C<sub>7</sub>H<sub>4</sub>O<sub>6</sub>Ni: N, 4.51. Found: 4.61.

The compound is of a light yellow color. It is soluble in boiling water, and also most common organic solvents. It dissolves in sodium hydroxide solution imparting to the latter a red color.

It was also found that the same acid was produced when 3-nitro-4-hydroxy-5-iodo-phenyl carbinol was oxidized in alkaline solution using an excess of potassium permanganate, since the melting point of the acid thus obtained was also 251°, and was not lowered by the addition of 3-nitro-4-hydroxy-5-iodo-benzoic acid, prepared by the method described above.

#### Summary.

1. The position of the mercury in the compound obtained by heating *p*-hydroxy-*m*-nitrophenyl carbinol has been established as *ortho* to the hydroxyl, *i. e.*, Position 5, and not *meta* to the hydroxyl, *i. e.*, Position 6, as assumed by Hart and Hirschfelder.

<sup>1</sup> Weselsky, *Ann.*, 174, 110 (1874).

2. The structure of 3-nitro-4-hydroxy-5-iodo-benzoic acid has been definitely established.

3. The preparation of 3-nitro-4-hydroxy-5-iodo-phenyl carbinol is described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY.]  
**THE SOLUBILITY OF PHTHALIC ACID IN WATER AND SODIUM  
SULFATE SOLUTIONS.**

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The purpose in undertaking this work was to determine the solubility of phthalic acid in water and in sodium sulfate solutions of different concentrations at different temperatures, because the literature records but few facts concerning the solubility of phthalic acid. Vaubel<sup>1</sup> gives the solubility of phthalic acid in water at 14° as 0.54 g. per 100 g. of solution. Graebe<sup>2</sup> gives its solubility at 99° as 18 g. per 100 g. of solution. In the preparation of phthalic acid it is often set free by treating its sodium salt with sulfuric acid and it was for this reason that its solubility was determined in sodium sulfate solutions. These solutions were made up to be 10 and 15% by weight.

The purity of the phthalic acid used was from 99.95%, with 0.02% ash, to 100%. No attempt was made to purify the acid further. It was supplied by the Monsanto Chemical Works. Pure anhydrous sodium sulfate was used. All solutions were prepared with water from which the carbon dioxide had been removed.

#### Experimental.

The method followed was somewhat similar to that of Walton and Judd.<sup>3</sup> The acid was put into 175 × 55 mm. heavy-wall glass tubes with the water or sodium sulfate solutions and agitated until equilibrium was attained. The tubes were immersed in a constant temperature water-bath which was controlled by a mercury-column regulator. At 25° a standardized thermometer reading from the -10° to +32° and graduated in 0.02° was used. For the higher temperatures a thermometer reading from -10° to +100° and graduated in 0.1° was used. The bath was kept constant to ±0.02°.

When equilibrium was reached the undissolved acid was allowed to settle and the saturated solution was drawn through an asbestos filter into a weighing tube (Fig. 1). Above 55° the solution was blown over into the weighing tube to prevent vaporization under the reduced pressure. The delivery tube was steam-jacketed to prevent crystallization of the acid in the tube (Fig. 2).

<sup>1</sup> Vaubel, *J. prakt. Chem.*, (2) **52**, 72 (1895); **59**, 30 (1899).

<sup>2</sup> Graebe, *Ann.*, **238**, 321 (1887).

<sup>3</sup> Walton and Judd, *THIS JOURNAL*, **33**, 1036 (1911).