[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF H. KOHNSTAMM AND COMPANY, INC.]

The Preparation of 2-Chlororesorcinol

BY ROBERT F. MILLIGAN AND FRED J. HOPE

Work undertaken in this Laboratory made it necessary to prepare 2-chlororesorcinol. A search of the literature failed to reveal any information for producing the compound. Likhosherstov and Zhabotinskaya[1] attempted its preparation by diazotizing 2-aminoresorcinol employing the Sandmeyer reaction; however, the diazotization of 2-aminoresorcinol produces 4-nitroso-2-diazo-resorcinol and not 2-chlororesorcinol.

An indirect method, however, was successful in forming the desired product. Hemmelmayr[2] showed that 3-bromo-5-nitro-β-resorcylic acid could be made to yield 3-bromo-β-resorcylic acid, and Rice[3] went a step further by decarboxylating the acid to produce 2-bromoresorcinol. Using these principles, the authors succeeded in preparing the corresponding chlorine analog in accordance with the following sequence: 5-nitro-β-resorcylic acid was converted by sulfuryl chloride to the corresponding 3-chloro compound which was reduced to the amino compound. This was diazotized and reduced by means of alkaline stannite and then decarboxylated to give 2-chlororesorcinol, m. p. 97–98° uncor.

Experimental

I. Chlorination of 5-Nitro-β-resorcylic Acid.—To a solution of 10 g. of 5-nitro-β-resorcylic acid in 50 cc. of glacial acetic acid, in a 150-cc., r. b. flask, 10 cc. of sulfuryl chloride was added. The condenser was attached and the mixture was slowly heated under reflux until it boiled. Refluxing was then continued for fifteen minutes at the expiration of which time 50 cc. of water was added. The mixture was allowed to stand and upon cooling the 3-chloro-5-nitro-β-resorcylic acid crystallized in long yellow needles. A single recrystallization from water yielded a product with m. p. 252° (with decompn.).

Anal. Calcd. for $C_7H_4O_6NCl \cdot H_2O$: Cl, 14.93. Found: Cl, 15.11.

II. Reduction of 3-Chloro-5-nitro-β-resorcylic Acid.—Five grams of 3-chloro-5-nitro-β-resorcylic acid was dissolved in 50 cc. of hot glacial acetic acid, and to this solution 50 to 60 cc. of stannous chloride solution (100 g. of stannous chloride in 100 cc. of hydrochloric acid) was added. Precipitation occurred almost immediately, and heating was continued for fifteen to twenty minutes on the steam-bath. The white crystalline material, after cooling, was removed by filtration employing suction and dissolved in about 100 cc. of boiling water. Upon cooling, brilliant colorless needles crystallized from the solution. The compound was removed by filtration and dried. Its m. p. was 220–222° (uncor.) with complete decomposition.

Anal. Calcd. for $C_7H_6O_4NCl \cdot HCl$: Cl, 29.55. Found: Cl, 29.81.

III. Diazotization of 3-Chloro-5-amino-β-resorcylic Acid.—A moist sample of the 3-chloro-5-amino-β-resorcylic acid was placed in a 250 cc. beaker and 50 cc. of water added. The mixture was heated to a boil and enough concd. hydrochloric acid added to bring about solution. The beaker was removed from the flame and while the solution was at or near the b. p. a solution of sodium nitrite (10% in water) was added drop by drop until a portion tested with starch–iodide paper showed an excess of nitrous acid. The solution was allowed to cool and bright yellow crystals of 3-chloro-5-diazochloride-β-resorcylic acid separated. These were removed by filtration and immediately reduced in accordance with the following method.

IV. Reduction of 3-Chloro-5-diazochloride-β-resorcylic Acid and Decarboxylation of 3-Chlororesorcylic Acid.—The crystalline mass of 3-chloro-5-diazochloride-β-resorcylic acid was dissolved in a solution of potassium hydroxide and treated with alkaline stannous chloride, prepared by dissolving 4 g. of stannous chloride in twice its weight of water and adding 40% potassium hydroxide until all the precipitate which had formed was redissolved. During the addition, effervescence occurred and nitrogen was liberated. After about half an hour the solution was acidified, then treated with an excess of concd. hydrochloric acid and refluxed for four hours. After cooling, the solution was extracted with ether, the ether washed with dilute sodium carbonate until clear and finally evaporated. The product remaining was crude 2-chlororesorcinol. The crystals were carefully purified by sublimation, m. p. 97–98°.

Anal. Calcd. for $C_6H_5O_2Cl$: Cl, 24.54. Found: Cl, 24.37.

Acknowledgment.—The authors wish to express their appreciation to their director, Mr. W. C. Bainbridge, and to Dr. W. F. Whitmore for their assistance.

Summary

A new compound, 2-chlororesorcinol, has been synthesized and characterized.

BROOKLYN, NEW YORK RECEIVED OCTOBER 19, 1940

---

[1] *J. Gen. Chem.* (U. S. S. R.), **2**, 761 (1932).

[2] Hemmelmayr, *Monatsh.*, **33**, 981 (1912); **35**, 1 (1914).

[3] Rice, THIS JOURNAL, **48**, 3125 (1926).