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The Synthesis of 2,7-Naphthalenedialdehyde; an Attempted Synthesis of Coronene

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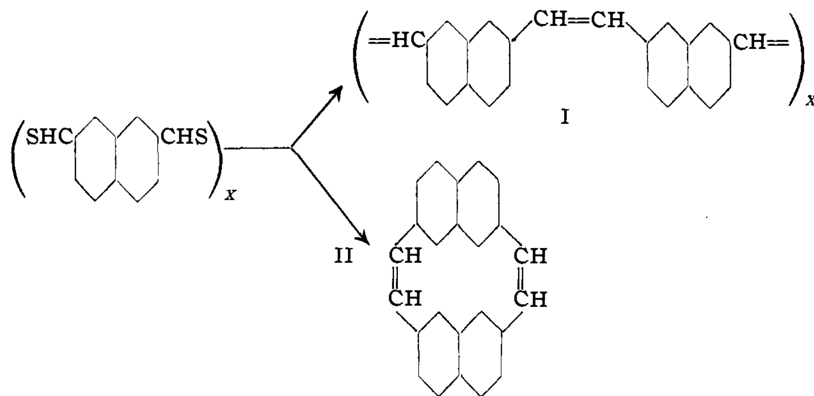
Although most of the 2,7-derivatives of naphthalene have been known for some time, the 2,7-dialdehyde has not been previously prepared. This aldehyde was synthesized by the Stephen[1] method wherein the corresponding 2,7-dinitrile was converted into the aldimine hydrochloride by the action of stannous chloride and hydrogen chloride in an ether solvent. The aldehyde was then obtained by hydrolysis. The structure of the aldehyde was established by the method of preparation, by oxidation by alkaline permanganate to the known 2,7-dicarboxylic acid, and by analysis of the aldehyde and its 2,4-dinitrophenylhydrazone.

The conversion of aryl thioaldehydes into stilbene analogs and homologs by heating with copper powder has been previously reported.[2] Such a conversion of 2,7-naphthalenedialdehyde might lead to two different types of ethylene derivatives as indicated



Ring closure of II by dehydrogenation at the alpha positions would give coronene.

Several attempts were made to prepare coronene as outlined above but all resulted in reaction products from which nothing definite was obtained. In this work, the thioaldehyde was readily prepared by the action of hydrogen sulfide upon naphthalenedialdehyde in the presence of hydrogen chloride. Upon heating the thioaldehyde with copper, non-sulfur containing materials were obtained. Attempts to convert this into coronene by heating alone and with selenium failed.

(1) Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

(2) Wood, Bacon, Meibohm, Throckmorton and Turner, THIS JOURNAL, **63**, 1334 (1941).

Experimental

Preparation of 2,7-Naphthalenedinitrile.—The method of Ebert and Merz[3] was followed, whereby the dinitrile was obtained by heating sodium 2,7-naphthalenedisulfonate with potassium cyanide. The yields in general were poor (10 to 15%).

Preparation of 2,7-Naphthalenedialdehyde.—Twelve grams of anhydrous stannous chloride and 150 ml. of dry ether were placed in a liter, three-necked flask equipped with a stirrer, reflux condenser, and an inlet for hydrogen chloride. Hydrogen chloride was bubbled in with stirring until solution of the stannous chloride was complete. This was indicated by the separation of a heavy, oily layer and the time required was about two and one-half hours. A suspension of 2 g. of 2,7-naphthalenedinitrile in 100 ml. of dry ether was then added with stirring over a period of forty minutes. Hydrogen chloride was passed in during this time. A viscous, yellow mass resulted. Stirring and the passage of hydrogen chloride were continued for a period of twenty-four hours by which time a yellow precipitate of the aldimine hydrochloride had formed. The mixture was cooled to zero before filtering to ensure as complete precipitation as possible. After filtration, the aldimine hydrochloride was hydrolyzed by refluxing in 250 ml. of water for twenty minutes. Upon cooling and filtering, the impure aldehyde mixed with inorganic material was obtained. Purification was partly accomplished through the bisulfite addition compound. Final purification was accomplished by two recrystallizations from water–alcohol solution which gave long, white needles, m. p. 142° (cor.). The yield was 0.5 g. (24.3%). 2,7-Naphthalenedialdehyde is soluble in methanol, ethanol, ether and benzene.

Anal. Calcd. for $C_{12}H_8O_2$: C, 78.26; H, 4.35. Found: C, 78.98; H, 4.19.

2,7-Naphthalenedialdehydedi-(2,4-dinitrophenylhydrazone).—The hydrazone was prepared from alcoholic solution catalyzed by a few drops of concd. hydrochloric acid. Recrystallization was not accomplished; color, orange; m. p., slight decomposition at 295°, complete decomposition at 312–313°.

Anal. Calcd. for $C_{24}H_{16}O_8N_8$: N, 20.59. Found: N, 20.13.

Summary

1. 2,7-Naphthalenedialdehyde was prepared by the action of stannous chloride on the corresponding dinitrile.

(3) Ebert and Merz, *Ber.*, **9**, 592 (1876).

2. The 2,4-dinitrophenylhydrazone of this aldehyde was prepared.
3. Attempts were made to obtain coronene by heating 2,7-polythionaphthalenedialdehyde with copper powder.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Factors Influencing the Cresolase Activity of Tyrosinase. The Effect of Gelatin and *p*-Cresol Concentration

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Previous workers[2,3,4] have demonstrated that tyrosinase preparations from the cultivated mushroom *Psalliota campestris* show a marked variation in ratio of catecholase to cresolase activity,[5] depending on the procedure used to isolate the enzyme. Since during the process of purification, unless special precautions are taken, the major portion of the cresolase activity is apt to be lost, the ratio of the catecholase to the cresolase activity in the purified preparation is often high (greater than 2). In these so-called "high catecholase" preparations, the catecholase activity is proportional to the copper in the preparation whereas the cresolase activity is not.[3,7] Until recently it was this type of preparation that was used for several investigations in this Laboratory concerning the nature, properties and mode of action of the enzyme tyrosinase.[2,7,8] In 1940 Parkinson and Nelson[4] reported the development of tyrosinase preparations in which the ratio of catecholase to cresolase activity was low (2 or less), and in which both enzymic activities were proportional to the copper content of the preparation. Such preparations have been called "high cresolase" preparations.

The development of different type tyrosinase preparations, having different ratios of catecholase to cresolase activities, has resulted in conjecture as to whether or not the enzyme is in reality one copper protein possessing two types of enzymic action, or is a mixture of two copper proteins each with its own activity. Before any considerable progress can be made toward a solution of this interesting and fundamental problem, it is necessary to have reliable means of characterizing the different type preparations on the basis of their catecholase and cresolase activities. Because of the marked inactivation of the enzyme that is observed particularly during the oxidation of catechol, it has been the practice to measure the enzyme activities in the presence of a "protecting" agent, gelatin being commonly used for this purpose.[2,9] Thus previous studies designed to compare the two types of tyrosinase preparations on the basis of their catecholase and cresolase activities have been made with gelatin present in the reaction medium.[4,10]

Recently, however, it has been found that the presence of gelatin in the reaction medium during the enzymatic oxidation of catechol (catecholase activity) tends to obscure fundamental differences between the different type preparations,[11] and it has been found that gelatin need not be present in the reaction medium in order to obtain a reliable measurement of catecholase activity.[12] These observations made it seem advisable to reinvestigate, from the same point of view, the effect of gelatin on the other characteristic activity of the different type tyrosinase preparations, *i. e.*, the cresolase activity.

The results of such a study, described in detail below, reveal that the increase in rate of oxidation of *p*-cresol (increase in cresolase activity), that is observed when tyrosinase is used in the

(1) Present address: Stamford Research Laboratories, American Cyanamid Company, Stamford, Conn.

(2) M. H. Adams and J. M. Nelson, THIS JOURNAL, **60**, 2474 (1938).

(3) D. Keilin and T. Mann, *Proc. Roy. Soc.* (London), **B125**, 187 (1938).

(4) G. G. Parkinson and J. M. Nelson, THIS JOURNAL, **62**, 1693 (1940).

(5) The ability of the enzyme preparation to catalyze the aerobic oxidation of the dihydric phenol catechol and the monohydric phenol *p*-cresol are referred to as catecholase and cresolase activities, respectively. One catecholase unit and one cresolase unit have been defined as the amount of enzyme required to cause the uptake of 10 cu. mm. of oxygen per minute when acting on 4 mg. of catechol and 4 mg. of *p*-cresol, respectively. For further details see Gregg and Nelson.[6]

(6) D. C. Gregg and J. M. Nelson, THIS JOURNAL, **62**, 2500 (1940).

(7) B. J. Ludwig and J. M. Nelson, *ibid.*, **61**, 2601 (1939).

(8) C. A. Bordner and J. M. Nelson, *ibid.*, **61**, 1507 (1939).

(9) M. H. Adams and J. M. Nelson, *ibid.*, **60**, 2472 (1938).

(10) D. C. Gregg and J. M. Nelson, *ibid.*, **62**, 2506 (1940).

(11) W. H. Miller and C. R. Dawson, *ibid.*, **63**, 3368 (1941).

(12) W. H. Miller and C. R. Dawson, *ibid.*, **63**, 3375 (1941).