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THE PREPARATION OF α-FURILDIOXIME

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The general interest in this laboratory in the use of the 1,2-dioximes in analytical chemistry (1) has naturally lead to a study of the methods of preparation of the various dioximes which have been proposed as analytical reagents. Following the original work of Soule (2) on the use of α-furildioxime as a reagent for nickel, there appear to be only two studies of the analytical applications of this reagent (3, 4). In a large measure this lack of interest derives from the difficulties in the preparation of the material and its consequent high price.

The synthesis of α-furildioxime involves the conversion of furfural to furoin by the acyloin condensation, the oxidation of the latter to furil by copper sulfate in pyridine, and the oximation of the furil. Hartman and Dickey (5) greatly improved the syntheses of furoin and furil but the last step has remained a serious stumbling block. The present paper deals with this last step.

Alpha-furildioxime was prepared by Macnair (6) along with some β-furildioxime by allowing furil to stand for several days or months in an alcoholic solution of hydroxylammonium chloride, and Soule (2) effected the oximation by refluxing an alcoholic solution of furil and hydroxylammonium chloride for five or six hours. Little is said about yield in either paper.

Our results with Soule's procedure were inconsistent and the yields ranged from one to twenty-three per cent. A series of oximations was carried out, varying singly the temperature, reflux time, and excess of hydroxylammonium chloride. No improvement in yield was obtained. Macnair (6) reported that α-furildioxime was converted to the β-form when heated to 150–160°, and that it was partially decomposed when heated in the presence of excess hydrochloric acid. Another series of experiments was conducted in which the excess hydrochloric acid was neutralized with calcium carbonate or sodium bicarbonate prior to removing the methanol, and in which the temperature was held below 90° throughout the procedure. The yields were again poor. Additional preparations were carried out using sodium hydroxylamine monosulfonate as an oximating agent, but these also were unsatisfactory.

Assuming that some side reaction competes seriously with the oximation reaction, it should be possible to favor the oximation by the slow addition of the furil to the hydroxylammonium chloride solution so that the latter is always greatly in excess. This scheme was found to give consistent and greatly increased yields. The details are given in the following recommended procedure.

EXPERIMENTAL

Alpha-furildioxime. In a 5-l. round-bottomed flask place 3200 ml. of technical-grade methanol, 208.5 g. (2.25 moles) of hydroxylammonium chloride, and a few boiling chips. Equip the flask with a 1500-ml. Soxhlet extractor[1] fitted with a suitable reflux condenser.

[1] Dr. C. F. H. Allen suggested the use of a hot Soxhlet extractor such as is described by Pingert, "Synthetic Organic Chemicals," Eastman Kodak Company, Rochester 4, N. Y., Vol. 18, No. 1, 1946.

Place a mat of glass wool in the bottom of the extractor and charge the extractor with 190 g. (1 mole) of purified furil. Heat the flask (most conveniently with an electric heating mantle and variable transformer) so that the alcohol boils vigorously and the methanol refluxes rapidly enough to fill the extractor at a rate of *ca.* 10 ml. per minute. Wrap a piece of asbestos paper around the siphon tube to prevent the furil from crystallizing in it.

As the extractor fills with methanol, the furil slowly dissolves and upon overflowing, 800 to 900 ml. of saturated alcoholic furil solution is added to the reaction flask. Within 10 to 15 minutes after the first furil has been added, the solution in the flask will turn straw yellow and continue to darken as the reaction proceeds and subsequent furil is added. Increase the heat input as necessary to maintain the reflux rate, but do not allow the temperature of the solution to exceed 95°. Continue the reaction until all of the furil has been transferred to the flask. Finally allow the extractor to fill and remove it and the alcohol in it from the flask. Remove the methanol by distillation under reduced pressure stopping the distillation when 500 to 800 ml. of viscous brown solution remains in the flask. After removing the bulk of the methanol do not allow the temperature to exceed 35°. Pour the reaction mixture into a 5-l. Erlenmeyer flask containing 600 ml. of water heated to 90°. Wash the flask with two 100-ml. portions of hot water. Boil the mixture until the crude tar goes into solution (usually 10–15 minutes). Remove the flask from the hot plate and add 100 to 150 g. of Norit previously boiled with dilute hydrochloric acid and, if it is already available, 3 to 5 g. of α-furildioxime to remove iron. Boil the mixture gently for 10 minutes and filter the boiling solution immediately, using a Büchner funnel and suction. Cool the solution under tap water or in an ice-bath. The solution turns milky and crystals of α-furildioxime separate. Filter the crude product on a Büchner funnel and spread it on wrapping paper to dry at room temperature. To recrystallize the product, if it is not white, dissolve it in the minimum of boiling water and treat with 50 g. of Norit as above. Yield 125–135 g., 54–56%; m.p. 84–85°, monohydrate. The melted material loses water and thereafter melts at 166–168°.

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