[Contribution from the Department of Chemistry, the University of Texas]

ATTEMPTED PREPARATION OF 3-HYDROXYFURAN BY THE METHODS OF HODGSON AND DAVIES

PHILIP S. BAILEY and J. VIRGIL WAGGONER

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Herein are described attempts to repeat the preparation of 3-hydroxyfuran as reported by Hodgson and Davies (1). The compound was desired in order to make alkoxy and other derivatives of it and thus gain support for or against the controversial (2) formulation of Hodgson and Davies (1).

We failed in the first step which consisted of the treatment of 2-furoic acid with bromine water to give a compound formulated by Hodgson and Davies (1) as 2-bromo-3-hydroxyfuran.[1] These authors used two methods. From the first method, reported earlier by Limpricht (3) and which employed the treatment of equal quantities of 2-furoic acid and water with bromine below 30°, we obtained only 5-bromo-2-furoic acid and water-soluble products. The second procedure, which differed from the first only in the amount of water and the presence of chloroform, yielded for us only 2,3,4,5-tetrabromotetrahydro-2-furoic acid and two unstable oils. The properties of these oils were different from those reported for the crystalline 2-bromo-3-hydroxyfuran, especially in that one was infinitely water-soluble and the other, though insoluble in cold water, decomposed in hot water to give water-soluble products. Hodgson and Davies (1) recrystallized their compound from water. They were also able to steam-distill it even in the crude oily form and in the presence of the acidic reaction medium. Due to its solubility in sodium carbonate solution and its failure to give positive ferric chloride tests, our water-insoluble oil is thought to be carboxylic rather than enolic in nature.

Each of the above procedures was repeated numerous times exactly as described by Hodgson and Davies (1) and also with variations from their procedure. The difference in our results and theirs must be due either to differences in the purity of the reagents used or incompletely described procedures. An effort to obtain further details concerning the reaction was not fruitful.

EXPERIMENTAL

Materials. The furoic acid, purified by several recrystallizations from water, melted at 132–133°. The bromine was Merck's Reagent grade; the chloroform, redistilled for several of the experiments, was General Chemical's U.S.P. grade; and the water was distilled.

Reaction of 2-furoic acid with bromine water by the chloroform method. The reaction was carried out at a temperature of 25–30° using 10 g. of furoic acid as described by Hodgson and Davies (1). After 100 ml. of cold water was added, the mixture was filtered and the resulting crystals were washed with cold water and dried; yield, 4.5 g., m.p., 154–156°. The filtrate was separated, the water layer was extracted with ether, the ether extract was added to the chloroform layer and the resulting solution was washed with cold water and evaporated, yielding a water-insoluble, unstable, yellow oil (7 g.). In several runs 11 g. (0.1 mole) of

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[1] A private communication from Professor George F Wright of the University of Toronto informs us that he, too, has been unable to carry out this reaction.

furoic acid was used (everything else, as before, 0.2 mole each); the yield of crystals was 9 g. and oil, 5 g. After several recrystallizations from benzene the melting point of the crystals increased to 159–160°. The material was identified as *2,3,4,5-tetrabromotetrahydro-2-furoic acid* as described later.

Anal. Calc'd for $C_5H_4Br_4O_3$: C, 13.91; H, 0.93.
Found: C, 13.93, 13.65; H, 1.57, 1.40.

In other runs, the following variations were made. The temperature was kept at 10° and 20° in two runs and no cooling was employed in another (temperature, 30–40°). Impure furoic acid (m.p. 127–129°), 10 ml. of water, tap water, traces of sulfuric acid, traces of calcium hydroxide, and chloroform saturated with water were used in other trials. In all these experiments, very little difference in results was noticed. Several runs were carried out with five times the usual amounts. Upon recrystallization of the crude tetrabromo compound, a water-soluble oil was obtained as a by-product.

The water-insoluble oil. The water-insoluble oil decomposed on standing, evolving hydrogen bromide and turning dark in color. The oil gave a negative ferric chloride test, was mostly insoluble in cold water, soluble in dilute sodium hydroxide and sodium carbonate solutions. Neutralization of these solutions gave only water-soluble materials. The oil decomposed in hot water (from the 11 g. runs, it partially crystallized to give 5-bromo-2-furoic acid, m.p. 185–186°) and during attempted steam-distillations yielding water-soluble products which reduced Fehling's solution and gave a negative ferric chloride test. Fehling-solution tests on the original oil were inconclusive due to the formation of a heavy precipitate. The oil could not be crystallized from common organic solvents, and it decomposed during attempted vacuum distillation.

The water-soluble oil. This material reduced Fehling's solution when heated, gave a positive Beilstein test for halogen, decomposed sodium carbonate solution, and gave a negative ferric chloride test. It completely resisted crystallization and slowly decomposed on standing, evolving hydrogen bromide and turning dark in color.

Reaction of 2-furoic acid with bromine water in absence of chloroform. A well-stirred suspension of 10 g. of 2-furoic acid and 10 g. of water was treated over a period of one hour with 30 g. of bromine at 25–30°. Fumes of hydrogen bromide were evolved and a yellow oil precipitated. The reaction mixture was poured into 150 ml. of cold water where colorless crystals formed (3 g., m.p. 184–186°). The filtrate was a clear solution which reduced Fehling's solution and turned dark on standing. Ether extraction of the filtrate or steam-distillation followed by ether extraction of the distillate yielded only a few additional crystals of the same material. The material was identified as 5-bromo-2-furoic acid as described later (m.p. 186–187° after water recrystallization).

Anal. Calc'd for $C_5H_3BrO_3$: C, 31.44; H, 1.58.
Found: C, 31.49; H, 1.94.

Variations in the procedure made use of crude furoic acid, tap water, and bromine mixed with 5 ml. of water. In the latter case, only an oil was obtained which resembled in behavior the water-insoluble oil described earlier.

5-Bromo-2-furoic acid. This substance was identified through its amide. A mixture of 1 g. of the acid and 5 ml. of thionyl chloride was refluxed for five minutes, cooled, and carefully poured into excess cold, concentrated ammonium hydroxide. The resulting crystals were filtered, washed, and recrystallized from aqueous ethanol solution; m.p. 141–143°. Hill and Sanger (4) reported 144–145°.

2,3,4,5-Tetrabromotetrahydro-2-furoic acid. This was identified by dehydrohalogenation according to the directions of Hill and Sanger (5) using alcoholic sodium hydroxide. The products were 4,5-dibromo-2-furoic acid (6) (m.p., 166–168°), 5-bromo-2-furoic acid (m.p. 186–187°), and 3,4-dibromo-2-furoic acid (m.p. 190–192°) as reported by Hill and Sanger (5).

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SUMMARY

2-Bromo-3-hydroxyfuran was not obtained from the treatment of 2-furoic acid with bromine water as reported by Hodgson and Davies. The only crystalline materials isolated were 5-bromo-2-furoic acid and 2,3,4,5-tetrabromotetrahydro-2-furoic acid.

AUSTIN, TEXAS

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