

Short Communications

Preparation of Furan from
cis-2-Butene-1,4-diol

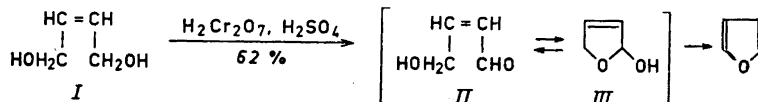
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According to Reppe *et al.*¹ catalytic dehydrogenation of *cis*-2-butene-1,4-diol (I) gives butyrolacton together with "appreciable amounts of furan". Apart from the reaction temperature (120°) and the composition of the catalyst no experimental data and no yields are reported.

Oxidation of butenediol with an aqueous solution of chromic acid-sulfuric acid gives a 62 % yield of furan. Evidently the reaction goes through the intermediate 4-hy-

butenediol) (20.0 g) and water (40 ml) are placed in a 250 ml reaction flask. The mixture is heated rapidly to 90°. Heating is discontinued and a solution of sodium dichromate (30.0 g of the dihydrate) in aqueous sulfuric acid (20 g of concentrated sulfuric acid in 70 ml of water) added dropwise with efficient stirring at such a rate, that the temperature is kept at 90–92°. A mixture of furan and water distills off immediately at a distillation temperature of 75–85°. Addition is complete after about 10 min. The mixture is then heated during 2–5 min to 100° (distillation temperature maximally 95°) to complete the reaction. The distillate consists of water (about 2 g) and impure furan (about 10 g). An impurity of the furan layer, detectable by its odor, is acrolein, which evidently has been formed by oxydation of allyl alcohol present as an impurity in butenediol. A 50 % aqueous solution of hy-



droxyisocrotonaldehyde (II), the cyclic semiacetal form of which (III) rapidly undergoes 1,4-elimination of water to give furan. Since the reaction takes place at 90°, furan distills off immediately, thereby evading the destructive influence of the acidic and oxidizing reaction mixture. Thus the first part of the reaction is a usual chromic acid oxidation of an allylic alcohol, while the following furanization reaction is similar to Quennehen and Normant's² quantitative transformation of 2-ethoxy-2,5-dihydrofuran into furan and ethanol under the influence of acidic reagents.

Experimental. Butenediol (purified product from General Aniline and Film Corporation, U.S.A., contains maximally 93 % of *cis*-

drazine (0.50 ml) is added to the distillate, and the resulting mixture shaken for 10 min at room temperature. All acrolein present in the furan layer is hereby removed. The mixture is now cooled to –20°, and the furan layer removed from the frozen aqueous layer by decantation and distilled from powdered potassium hydroxide (2.5 g). Furan (8.94 g, b.p. 31°, n_D^{20} 1.4208) is obtained as the only fraction. The yield, based upon pure *cis*-butenediol, is 62 %, or higher.

1. Reppe, W. *et al.* *Ann.* **596** (1955) 159, 182.
2. Quennehen, F. and Normant, H. *Compt. rend.* **228** (1949) 1301.

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