A Simple Preparation of 2-Butenolide

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In recent years there has been increasing interest in the application of 2-butenolide as a key intermediate for the

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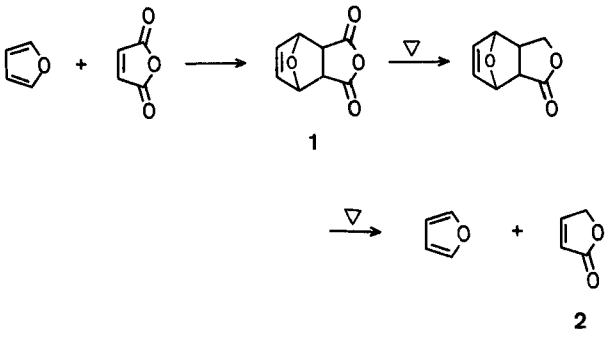
synthesis of a variety of natural products[1,2,3]. Although several methods for the preparation of this exceptional Michael acceptor have been reported in the literature[4,5] no simple procedure for the synthesis of this lactone is available; current synthetic methods involve multi-step processes and afford low to moderate yields of the desired compound **2**.

Takano and Ogasawa[6] have recently demonstrated an improved synthesis of **2** from the thermolysis of the reduced tricyclic anhydride **1**.

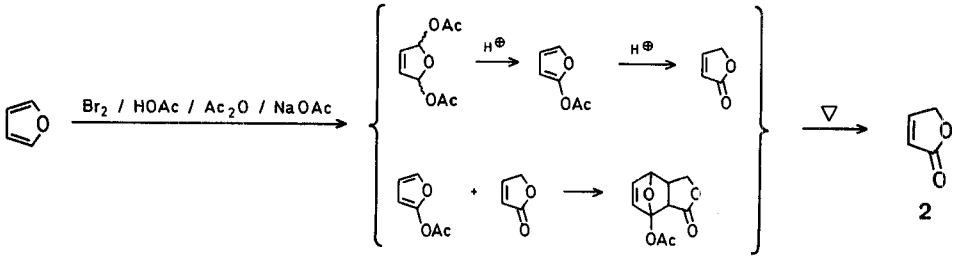


1

2

This method, although affording good yields of the desired compound, involves three isolation steps and cannot be completed within one afternoon.

We wish to report a rapid and convenient synthesis of 2-butenolide (**2**) by a modification of a procedure first utilized by Clauson-Kaas and Elming for the preparation of 2,5-diacetoxy-2,5-dihydrofuran[7].



We have found that when furan is added to a solution of bromine in acetic acid/acetic anhydride/sodium acetate at 30° and maintained between 30° and 50° a black tar results which, upon thermolysis affords 2-butenolide (**2**) in good yield. Formation of this product is easily rationalized by the reaction sequence depicted above[8].

Preparation of 2-Butenolide (2):

To a solution[9] of anhydrous sodium acetate (51 g), acetic acid (100 ml), and acetic anhydride (150 ml) is added bromine (40 g, 0.25 mol). The resultant mixture is put under nitrogen and furan (20 ml, 0.27 mol) is added such that the temperature of the reaction mixture is maintained between 30° and 50°. The mixture is cooled to 0° for 30 min followed by heating in a water bath at 80° in the course of 45 min, kept at 80° for 5 min, and cooled to room temperature. The sodium bromide is removed by filtration and washed with acetic acid (50 ml) containing 10% acetic anhydride. The filtrate is evaporated on a water bath at 70°/12–16 torr. When the distillation is complete a dark green oil remains in the flask. Ether (50 ml) is then added, and the precipitate is removed by filtration. The etheral solution is evaporated and the resultant oil is distilled through a Claisen head containing a 4 cm condenser; after the collection of 1–2 ml of 2-butenolide at 85–103°/12–16 torr distillation ceases. The remaining black residue is pyrolyzed in vacuo (12–16 torr) with a heat gun or bunsen burner until distillation ceases to afford 15–18 g of crude, yellow-brown lactone. The two fractions are combined and redistilled from a catalytic amount of potasium carbonate; the 2-butenolide is collected; yield: 13–15 g (62–71%); b.p. 96–98°/20 torr (Lit.[4] b.p. 96–98°/20 torr).

H.P.L.C. analysis utilizing a 2 ft × 1/8 in analytical column containing μ poracil or coracil type II and eluting with chloroform indicates the presence of only one component.

I.R. ($CHCl_3$): ν_{max} = 1783, 1751 cm^{-1} (C=O).

^{1}H-N.M.R. ($CDCl_3$): δ = 4.92 (t, 2H); 6.15 (2t, 1H); 7.63 ppm (2t, 1H).

M.S. (20 eV): m/e = 84 (M^+, 38%); 55 (100%).

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[8] Attempts to isolate proposed intermediates were unsuccessful.
[9] Care should be taken when dissolving anhydrous sodium acetate in acetic acid/acetic anhydride as a great deal of heat is evolved.

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