An Improved Synthesis of γ-Crotonolactone (2-Buten-4-olide)

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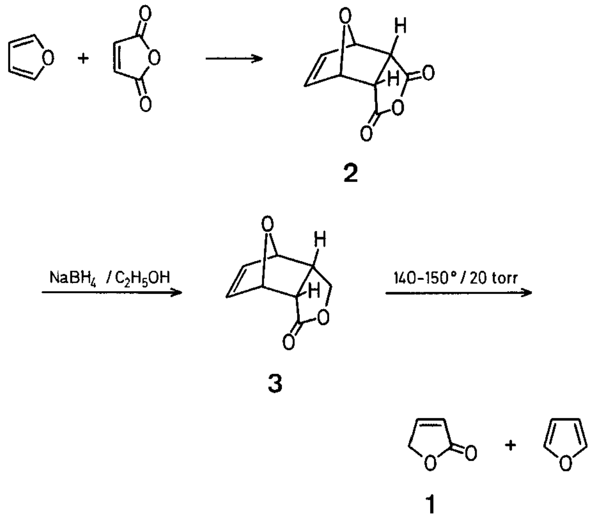
γ-Crotonolactone (**1**) is the simplest example of the butenolide ring-system, which occurs in many physiologically active natural products and is an interesting compound because of its reactivity. Although its chemical structure looks rather simple, no satisfactory procedure for the preparation of this lactone (**1**) has been reported. The initial synthesis [1-4], involving a five-step sequence from epichlorohydrin and sodium cyanide, gave an overall yield of 25%.

Glattfeld et al.[5], used a shorter route from glycerol chlorohydrin and sodium cyanide, consisting of hydrolysis and distillation of the intermediate dihydroxy acid to form γ-crotonolactone in 23% yield.

The best method[6], hitherto known, has been described in *Organic Synthesis* reporting an overall yield of 33%. However, this route contains a vexatious step with handling of α-bromo-γ-butyrolactone which can cause severe eye and skin irritation.

The necessity of γ-crotonolactone (**1**) as a synthetic intermediate has led us to investigate some alternative routes, as a result of which an improved new procedure for the synthesis of the lactone (**1**) has been found.

Thus, by applying the result[7] that some cyclic acid anhydrides are reduced into the corresponding lactones, the tricyclic anhydride (**2**)[8] was reduced into the tricyclic lactone (**3**) in 80% yield. And then, a retro-Diels-Alder reaction of the tricyclic lactone (**3**) was successfully carried out at 140–150° under a reduced pressure to afford γ-crotonolactone (**1**) in an excellent yield of 78.6% (Overall yield; 65.2%).



The Tricyclic Lactone (3):
To a suspension of the anhydride (**2**)[8], (24.9 g, 0.15 mol) in ethanol (300 ml) was added in small portions sodium borohydride (7.56 g, 0.2 mol) with stirring and cooling in an ice bath. The reaction mixture was allowed to come slowly to 20° by permitting the ice in the cooling bath to melt. Two hours after the addition of the sodium borohydride had been completed, the reaction mixture was cooled to 0° and acidified with 10% hydrochloric acid to pH 2. After removal of nearly all of the ethanol, the residue was extracted with dichloromethane, the extract washed successively with water, 5% sodium hydrogen carbonate, and water, and dried over anhydrous sodium sulfate. The crystalline solid remaining after removal of sodium sulfate and dichloromethane was recrystallised from benzene to yield the tricyclic lactone (**3**) as colorless needles; yield: 18.3 g (80%); m.p. 98.0°.

$C_8H_8O_3$	calc.	C 63.15	H 5.30
	found	62.92	5.34

γ-Crotonolactone, 2-Buten-4-olide (1):
The tricyclic lactone (**3**; 7.6 g, 50 mmol) was heated with stirring under a reduced pressure (20 torr) until the temperature of an oil bath reached 140–150°. The retro-Diels-Alder reaction of the lactone (**3**) took place with violent evolution of gaseous furan[9] to give γ-crotonolactone (**1**); yield: 3.3 g (79%); b.p. 96–98°/20 torr. Overall yield; 65.2%. The data of I.R. and N.M.R. spectra were in agreement with that described in the literature[6].

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[9] Furan was recovered in about 80% yield by using a trap chilled with dry ice-acetone.