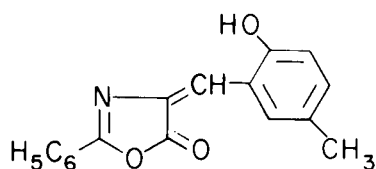


Department of Chemistry, University of Cincinnati

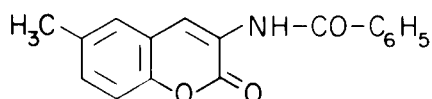
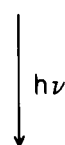
## Substituted $\gamma$ -Lactones. XXII (1,2). The Reaction of 2-Phenyl-4-(2-hydroxy-5-methylbenzylidene)-5-oxazolone with Light

Roderich Walter (3), Thomas C. Purcell (3) and Hans Zimmer

Previously this laboratory reported the light-induced cyclization of  $\alpha$ -(2-aminobenzylidene)- and  $\alpha$ -(2-hydroxybenzylidene)- $\gamma$ -butyrolactones (4, 5). In the present note we should like to report on the photochemical conversion of 2-phenyl-4-(2-hydroxy-5-methylbenzylidene)-5-oxazolone (I) (6) to 3-benzamido-6-methylcoumarin (II).



I



II

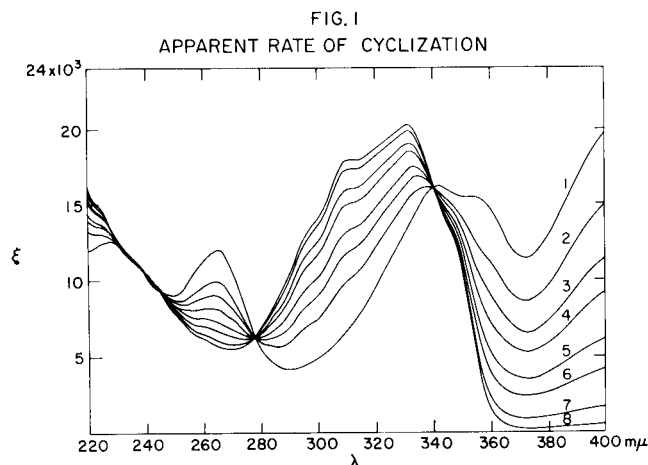
Isosbestic points were observed (Figure I) when I was converted to II by irradiation with light. As this coincides with earlier observations during the cyclization of  $\alpha$ -substituted  $\gamma$ -lactones (4, 5), we should like to believe that 2-phenyl-4-(2-hydroxy-5-methylbenzylidene)-5-oxazolone also cyclizes after *trans-cis* isomerization through a nucleophilic attack of the hydroxy group on the carbonyl carbon to yield the 3-benzamido-6-methylcoumarin. The present data do not, however, exclude the possibility that the cyclization of the substituted oxazolone is merely

due to an increase in the nucleophilicity of the phenolic hydroxyl group of the photochemically excited species.

TABLE I

Apparent Rate of Cyclization of Compound I  
at  $47.00 \pm 0.05^\circ\text{C}$

Curve No.	Time Min.	E(Absorbance) 312 m $\mu$	Concentration Moles/Liter
1	0	0.72	$1.00 \times 10^{-4}$
2	30	1.03	$0.70 \times 10^{-4}$
3	50	1.21	$0.53 \times 10^{-4}$
4	60	1.34	$0.43 \times 10^{-4}$
5	80	1.52	$0.27 \times 10^{-4}$
6	90	1.61	$0.19 \times 10^{-4}$
7	120	1.74	$0.07 \times 10^{-4}$
8	150	1.80	$0.00 \times 10^{-4}$



## EXPERIMENTAL (7)

## Kinetic Measurements.

Compound I ( $1.00 \times 10^{-4} M$  solution in 95% ethanol) was placed in a round-bottom, three-necked flask. This reaction vessel was fitted with a condenser, thermometer, and quartz immersion well. A magnetic stirrer was used for continuous agitation of the reaction mixture, which was irradiated with a 75-watt General Electric lamp (FG 1096 AX) placed into the water-cooled quartz immersion well (8). The reaction vessel with its light source, surrounded by a constant temperature water-bath (Tecan Tempunit, ASL 414-60), was employed for kinetic studies. At timed intervals a sample was pooled and its absorption spectrum was recorded in the range of 220  $m\mu$  to 400  $m\mu$  (Figure 1). By means of the method of half-lives (9) the apparent rate constant of the light-induced reaction was determined under the experimental conditions as  $0.0132 \text{ min}^{-1}$  ( $\tau = 52.5$  minutes) (Table I). After completion of the reaction the solvent was evaporated. The resulting slightly yellow crystals melted at  $169^\circ$  and a mixed melting point with authentic material of 3-benzamido-6-methylcoumarin showed no depression (6).

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Received February 5, 1966

Cincinnati, Ohio 45221