

Photolysis of *cis*-Tetrahydrobenzopyran-2-ones. Intramolecular Cycloaddition and a Photo-ene Reaction

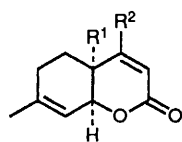
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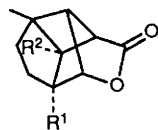
Photolysis of the bicyclic lactones (1) and (2) leads to products from intramolecular cycloaddition and photo-ene reaction.

The intramolecular [2 + 2] photocycloaddition of cyclic α,β -enones with a remote double bond has in recent years become a useful synthetic method for the construction of complex carbocyclic systems *en route* to natural product synthesis.¹ Despite the plethora of examples of such intramol-

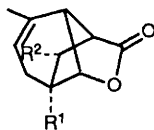
ecular additions involving an enone and alkene there have been few reports relating to intramolecular alkene cycloaddition to an α,β -unsaturated lactone.² The examples have been restricted to flexible models with the alkene unit present in a side chain. We now report on the photolysis of the bicyclic



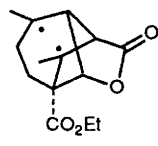
- (1) $R^1 = \text{CO}_2\text{Et}$, $R^2 = \text{Me}$
 (2) $R^1 = \text{Me}$, $R^2 = \text{H}$



- (3) $R^1 = \text{CO}_2\text{Et}$, $R^2 = \text{Me}$
 (5) $R^1 = \text{Me}$, $R^2 = \text{H}$



- (4) $R^1 = \text{CO}_2\text{Et}$, $R^2 = \text{Me}$
 (6) $R^1 = \text{Me}$, $R^2 = \text{H}$



(X)

lactones (1) and (2), rigid examples of such a system, leading to intramolecular cycloaddition and a photo-ene reaction.

The lactones (1) and (2) were prepared in connection with an approach to the synthesis of trichothecene sesquiterpenes.³ The *cis*-ring junction in these lactones brings the two double bonds in proximity, and we therefore studied the possibility of intramolecular cycloaddition to generate novel structural types. Photolysis of an acetone solution (or benzene solution with added acetophenone) of (1) using a Hanovia 450 W mercury lamp afforded the cycloadduct (3) and the rearranged product (4) in 2 : 3 proportion in 80% combined yield [based on *ca.* 20% recovered (1) after 8 h reaction]. These were

separated by PLC and (4) was obtained as a solid, m.p. 75–77 °C; ν_{max} , 1780 and 1725 cm^{-1} ; $^1\text{H NMR}$ δ 1.11 (d, 3H), 1.26 (t, 3H), 1.71 (dd, 3H), 2.48 (m, 3H), 2.70 (m, 1H), 2.88 (m, 1H), 4.18 (q, 2H), 4.71 (br s, 1H), and 5.40 (m, 1H); $^{13}\text{C NMR}$ δ 175.78, 172.12, 132.11, 120.31, 82.27, 60.88, 55.81, 53.03, 50.81, 38.20, 37.82, 21.89, 14.87, and 14.18; m/z 250.1197 ($\text{C}_{14}\text{H}_{18}\text{O}_4$). The formation of (4) corresponds to a photo-ene reaction⁴ and can be rationalised as proceeding *via* an intermediate biradical (X) and hydrogen transfer. The configuration of the secondary methyl group is assigned from the possible mode of hydrogen transfer in a six-membered transition state. The cycloadduct (3) showed IR, ν_{max} , 1780 and 1725 cm^{-1} ; $^1\text{H NMR}$ δ 1.20 (s, 6H), 1.28 (t, 3H), 4.23 (q, 2H), and 4.7 (m, 1H). Similar photolysis of (2) furnished (5) and (6) in a 3 : 2 proportion. The greater proportion of the ene product in the case of (1) is attributable to the presence of the methyl group which stabilises the radical.

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