

PHOTOCHEMISTRY OF ESTERS II. EFFECTS OF RING SIZE ON  
THE PHOTOCHEMICAL BEHAVIOR OF  $\alpha,\beta$ -UNSATURATED ESTERS

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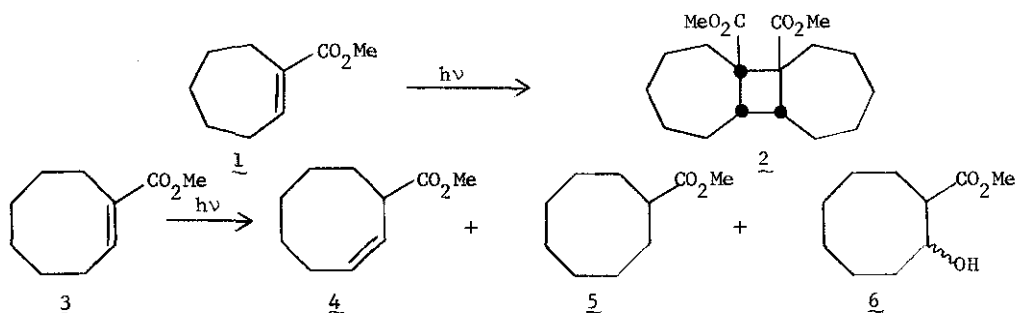
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As a part of our investigation of the photochemistry of  $\alpha,\beta$ -unsaturated esters,<sup>1</sup> we have initiated studies on the photochemical behavior of methyl-1-cycloheptene and cyclooctene carboxylates. The chemistry of these compounds differs markedly from that of acyclic,<sup>2</sup> cyclopentene,<sup>1</sup> and cyclohexene<sup>3-5</sup> esters. This report describes our preliminary results, and considers some mechanistic implications for ester photochemistry.

Irradiation of 1 in pentane solution through Vycor with a 450W mercury lamp resulted in rapid disappearance of starting material, and the formation of two major products in a ratio of about 14:86, as determined by gas chromatographic analysis. Chromatography on alumina followed by crystallization gave the major product, m.p. 102-103°C, in 42% yield. The minor product was isolated in small amount by preparative gas chromatography. Both of these compounds gave mass spectra and <sup>1</sup>H and <sup>13</sup>C magnetic resonance spectra which are in good accord with cyclobutane dimers of starting ester. The stereochemistry of the minor dimer remains undetermined, while that of the major dimer was established as head to head-trans-anti-cis, 2, as evidenced by x-ray diffraction studies. No evidence could be found for deconjugated ester.

Compound 2 is monoclinic Cc,  $a = 16.40(1)$ ,  $b = 8.549(6)$ ,  $c = 13.64(1)\text{Å}$ ,  $\beta = 117.03(4)^\circ$ ,  $Z = 4$ . Of the 1074 independent reflections ( $2\theta_{\text{max}} = 100^\circ$ , Cu  $K_\alpha$  radiation), 893 reflections were employed in the solution and refinement of the structure. The crystal structure consists of discrete molecules of 2 with no unusual intermolecular contacts. The dihedral angle for the central ring in 2 is  $158^\circ$ . The average C-C distance is  $1.56\text{Å}$  and the average C-C-C angles are  $113^\circ$  for the cycloheptane rings and  $88^\circ$  for the cyclobutane rings. The isotropic refinement is presently at a conventional R of 0.11.

Irradiation of 3 under identical conditions resulted in slow transformation to the cis-deconjugated isomer 4 in 70% yield. Reduced and hydroxylated compounds 5 and 6, were also formed in about 4% and 1% yields, respectively. No evidence of dimer formation was obtained.



There is ample precedent for the intermediacy of trans-olefin or its equivalent in the photochemical transformations of 6-, 7-, and 8-membered cyclic olefins and in the 6-membered ester.<sup>6</sup> Examination of molecular models of trans 1 and 3 reveals that the  $\gamma$ -hydrogen atoms should be readily accessible to the carbonyl oxygen. It seems probable that, if trans-olefin is formed, then deconjugation would be observed. This appears to be true for 3, the only other significant product being a small amount of 5, which presumably results from hydrogen abstraction from solvent. We feel that formation of 4 is good evidence for the intermediacy of trans-3, and that in the 8-membered ring the trans-olefin has sufficient thermal stability to show photochemical behavior similar to that of acyclic systems. The expected product of this process is trans-4, but no evidence for the formation of trans-olefin was observed in infra-red spectra of irradiated solutions. Isomerization to the more stable cis-4 could easily occur by a photochemical process.

The highly stereoselective formation of 2 strongly suggests the intermediacy of trans-1, which could undergo thermal or photocycloaddition with cis-1. Attempts to trap trans-1 by irradiating 1 in the presence of 10-fold excesses of methanol, furan, and cyclopentene were unsuccessful; only the dimers were obtained as before. The absence of mixed adducts argues against radical and ionic intermediates in the dimerization, and suggests the intervention of a complex. Examination of the uv absorption spectra of 1 in solvents of differing polarity and over a wide concentration range revealed no evidence for ground state complexation, suggesting the formation of an exciplex. We are presently extending the trapping experiments to lower temperatures in attempts to determine the presence of trans-1, and to look for trans intermediates in irradiations of 3.

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