

## A New Photochemical Reaction of Cyclopentenones

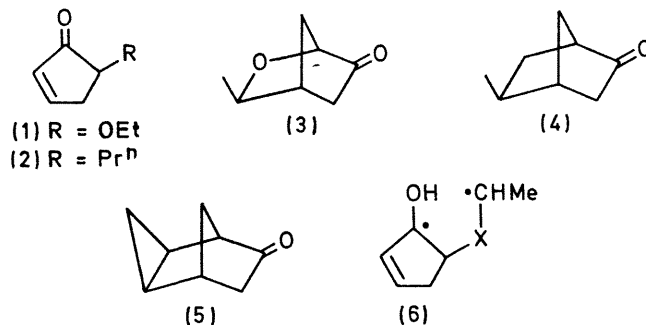
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**Summary** Irradiation of 5-ethoxycyclopentenone (**1**) and 5-propylcyclopentenone (**2**) leads to *exo*-3-methyl-2-oxabicyclo[2,2,1]heptan-6-one (**3**) and *exo*-5-methylnorbornan-2-one (**4**), respectively.

We report here a photochemical isomerization observed in two cyclopentenones which leads to formation of bicyclic ketones. Irradiation ( $\lambda > 2800 \text{ \AA}$ ) of 5-ethoxycyclopentenone (**1**)<sup>1</sup> in methanol solution gives (ca. 17%) *exo*-3-methyl-2-oxabicyclo[2,2,1]heptan-6-one (**3**) plus at least five other products which will be described later. The structure of (**3**) was deduced from its spectroscopic properties: i.r.  $1768 \text{ cm}^{-1}$ ; n.m.r. (220 MHz)  $\delta$  1.19 (d,  $J$  6 Hz, 3H), 1.56 (dd,  $J_1$  11,  $J_2$  ca. 2 Hz, 1H), 1.86 (dd,  $J_1$  17,  $J_2$  4 Hz, 1H), 1.99 (m,  $J_1$  11,  $J_2$  4,  $J_3$  ca. 2 Hz, 1H), 2.06 (dd,  $J_1$  17,  $J_2$  4 Hz, 1H), 2.45 (m,  $J_1$  4,  $J_2$  ca. 2 Hz, 1H), 3.79 (q,  $J$  6 Hz, 1H), 3.93 (d,  $J$  2 Hz, 1H). A similar transformation occurred on photolysis of 5-propylcyclopentenone (**2**), which was prepared by bromination-dehydrobromination of 2-propylcyclopentanone using the procedure of Garbisch.<sup>2</sup> In this case irradiation ( $\lambda > 3320 \text{ \AA}$ ) produced at least four products, the major one (44%) of which was *exo*-5-methylnorbornan-2-one (**4**). The structure of (**4**), deduced from spectroscopic data, was confirmed by independent synthesis. (**5**)<sup>3</sup> absorbed two equivalents of hydrogen over platinum to yield both *exo*-5- and *exo*-6-methylnorbornan-2-ol, which

were separated by g.l.c. of the derived acetates. Subsequent saponification and Jones oxidation<sup>4</sup> gave (**4**).



A possible pathway for these reactions is through the well-known type II biradical (**6**)<sup>5</sup> formed on abstraction of  $\gamma$ -hydrogen by carbonyl oxygen. Cyclization of this intermediate at the double bond can produce the desired isomer directly as its enol. In each case only *exo*-isomers were found; in models, closure of (**6**) to the *endo*-compounds appears sterically less likely.

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<sup>1</sup> C. H. DePuy, R. D. Thurn, and M. Isaks, *J. Org. Chem.*, 1962, **27**, 714.<sup>2</sup> E. W. Garbisch, jun., *J. Org. Chem.*, 1965, **30**, 2109.<sup>3</sup> K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 1965, **30**, 2278.<sup>4</sup> A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 1953, 2548; C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, 1956, **21**, 1547.<sup>5</sup> J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, ch. 5.