Photoisomerization of 2-(Hept-6-enyl)cyclopent-12-enones to Tricyclo[7.3.0.0^{1,7}]dodecan-12-ones

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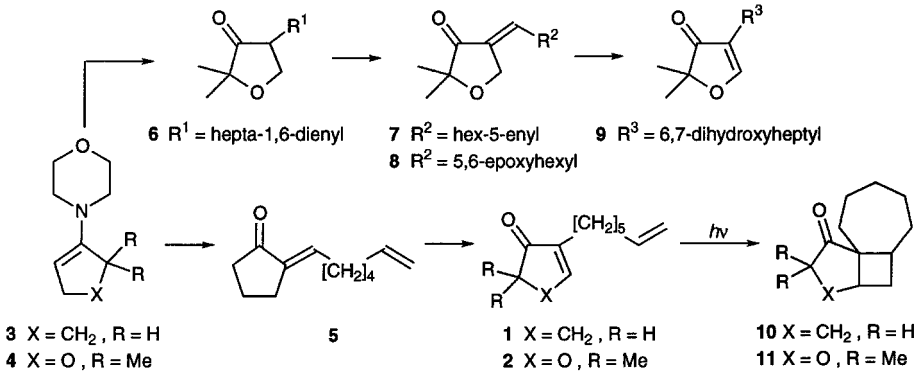
Rolf Christoph Gebel and Paul Margaretha*

Institut f. Organische Chemie der Universität, D-20146 Hamburg, Germany

On irradiation ($\lambda > 340$ nm), the newly synthesized 2-(hept-6-enyl)cyclopent-2-enones **1** and **2** isomerize selectively to the *straight* cycloadducts (tricyclo[7.3.0.0^{1,7}]dodecan-12-ones) **10** and **11**, respectively.

Reports on the photoisomerization of 2-alkenylcycloalk-2-enones to tricycloalkanones have up to now been limited to cyclopent-2-enones or cyclohex-2-enones bearing either a but-3-enyl or a pent-4-enyl side chain on C(2).[1] We now report on the synthesis of two novel five-membered enones bearing a hept-6-enyl side chain on C(2) (**1** and **2**) and on their photochemical behaviour.



Enamines **3** and **4** reacted with hept-6-enal to afford ketones **5** and **6**, respectively. The migration of the exocyclic C=C double bond into the five-membered ring was achieved either by heating with HCl in butanol (**5**→**1**) or with $RhCl_3$ in ethanol[7] (**7**→→**2**). In this latter sequence the terminal C=C double bond was protected as an oxirane (**8**), which was cleaved by $RhCl_3$ to a vicinal diol (**9**). Reductive bis-elimination of OH^- using imidazole, chlorodiphenylphosphine, iodine and zinc[8] afforded the terminal alkene **2**.

Irradiations of **1** and **2** in benzene using 350 nm lamps with a cut-off filter < 340 nm proceeded very slowly, requiring *ca*. 15 days for the conversion of 10^{-3} mol, and led to the formation of only one photoproduct (**10** and **11**) in each case in very low isolated yields (6 and 10%, respectively). This sluggishness in cyclization as compared to the efficient conversion of 2-(pent-4-enyl)cyclopent-2-enones to tricyclodecanones reflects the long-known rate difference in cyclization for an oct-7-enyl radical and a hex-5-enyl radical,[9] respectively.

Techniques used: ^{1}H NMR, ^{13}C NMR, ^{1}H,^{1}H-COSY NMR, ^{1}H,^{13}C-COSY NMR, MS

References: 15

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*To receive any correspondence.

References cited in this synopsis

1 M. T. Crimmins and T. L. Reinhold, *Org. React. (N.Y.)*, 1993, **44**, 297.
7 J. Andrieux, D. R. R. Barton and H. Patin, *J. Chem. Soc., Perkin Trans. 1*, 1977, 359.
8 Z. Liu, B. Classon and B. Samuelsson, *J. Org. Chem.*, 1990, **55**, 4273.
9 A. L. J. Beckwith and G. Moad, *Chem. Commun.*, 1974, 472.