Synthetic Organic Photochemistry: Photochemical Approach to Hydroazulenes by Photolysis of a βγ-Unsaturated Ketone

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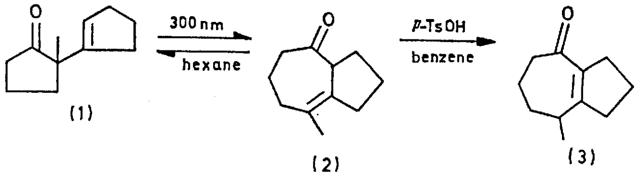
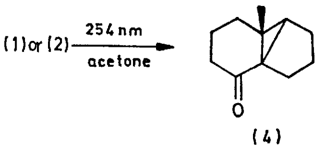
Summary Direct irradiation of 2-methyl-2-(cyclopent-1-enyl)cyclopentanone (**1**) gives the hydroazulene (**2**), whereas the tricyclic ketone (**4**) is produced upon sensitized irradiation in acetone.

We report a method for the construction of the hydroazulene ring system which utilizes the photochemical 1,3-acyl shift rearrangement typical of $\beta\gamma$-unsaturated ketones.[1] In the case examined, this photochemical rearrangement produces a hydroazulene derivative containing several of the structural features characteristic of some of the hydroazulene class of sesquiterpenes, *e.g.*, bulnesol.

Compound (**1**)† was prepared by methylation of 2-cyclopentylidenecyclopentanone with potassium t-butoxide and methyl iodide. Photolysis of (**1**) in hexane with 3000 Å light produced a single photoproduct in approximately 50% yield based upon recovered (**1**). The structure of the new product was established as (**2**) [ν_{max} (CCl_4) 1705 cm^{-1}; δ 1·61 (3H, s), 3·80 (1H, m) and 1·95—2·45 (12H, m)]. The photolysis of a pure sample of (**2**) in hexane produced the same mixture of (**1**) and (**2**) as in the direct photolysis of (**1**) indicating that the reaction is readily reversible. In contrast to the above results, photolysis of (**1**) in acetone gave the tricyclic ketone (**4**) [ν_{max} 1670 cm^{-1}; δ 1·07 (3H, s), 2·50—2·90 (2H, m); λ_{max} (iso-octane) 278 nm (ϵ26)].





The photolysis of the hydroazulene (**2**) in acetone also gave (**4**) as the only detectable product. However, the relative rate of this transformation was lower than the rate of conversion of (**1**) into (**4**). From the results of these

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† All new compounds gave satisfactory analytical results and had the expected spectral data.

experiments it appears that (**1**) behaves according to the predictions based upon an increasing number of studies of the photochemistry of $\beta\gamma$-unsaturated ketones.[1–4] The separation of singlet–triplet reactivity into the 1,3-acyl migration *versus* oxa-di-π-methane rearrangement is maintained.[1] The oxa-di-π-methane rearrangement in the sensitized reaction of (**2**) is in accord with recent results of Hancock and Grider,[2] Engel and Schexnayder,[3] and others in that the excited state triplet energy cannot be simply dissipated by *cis* and *trans* isomerization of the cyclopentene double bond. The third type of photochemical reaction, δ-hydrogen abstraction, sometimes observed with $\beta\gamma$-unsaturated ketones is not found in this system.[4] Finally, the interaction of the two chromophores in (**1**), a requirement suggested by Williams and Sarkisian,[5] is demonstrable by u.v. analysis of the starting ketone [λ_{max} (iso-octane) 323(ϵ63), 313(120), 311(120), 302(129), 287(105), 258(342)].

Of particular interest is the oxa-di-π-methane rearrangement of the seven-membered hydroazulene (**2**). This reaction proceeds smoothly under the conditions used for the (**1**) → (**4**) rearrangement and contrasts with the recent results by Williams and Sarkisian[5] on a cyclohept-3-en-1-one system for which only the 1,3-acyl migration was found.

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