Journal of

The Chemical Society,

Chemical Communications

NUMBER 4/1973 21 FEBRUARY

Intramolecular Photocycloaddition of 3-(But-3-enyl)oxy- and 3-(Pent-4-enyl)oxy-cyclohex-2-enones: Stereospecific Formation of 2-Oxabicyclo-[3,2,0]heptane and -[4,2,0]octane Systems

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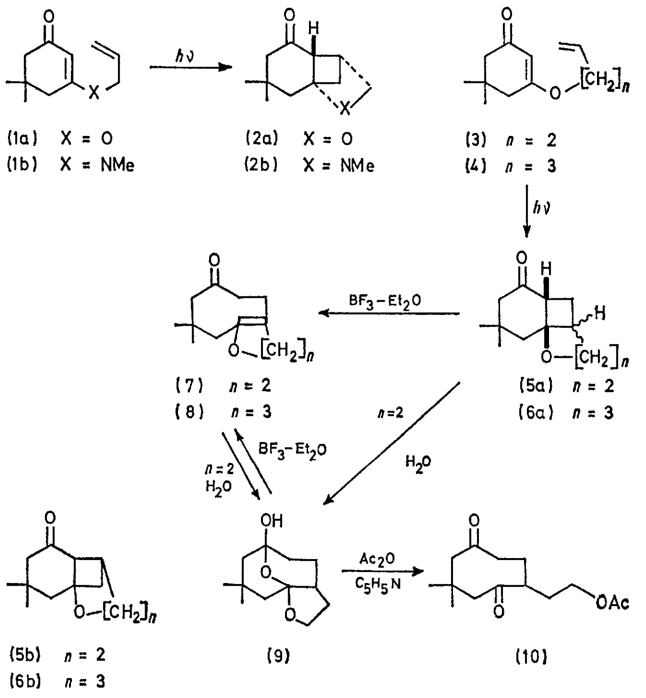
Summary Irradiation of 3-(but-3-enyl)oxy- and 3-(pent-4-enyl)oxy-cyclohex-2-enones results in an intramolecular cycloaddition to afford stereospecifically 2-oxabicyclo-[3,2,0]heptane and -[4,2,0]octane systems, respectively.

The intramolecular photocycloaddition reactions of non-conjugated dienes have been extensively investigated.[1] We have recently reported the photochemical conversion of the related 3-allyloxy- and 3-allylamino-cyclohex-2-enones (**1a**) and (**1b**) into the 2-oxa- and 2-aza-bicyclo-[2,1,1]hexane systems (**2a**) and (**2b**).[2] We have investigated the photochemical behaviour of the homologous systems, 3-(but-3-enyl)oxy- (**3**) and 3-(pent-4-enyl)oxy-5,5-dimethylcyclohex-2-enones (**4**) and report here that the cycloaddition occurs in a stereospecific manner to give the 2-oxabicyclo[*n*,2,0] systems rather than the 2-oxabicyclo-[*n*,1,1] systems.

Compounds (**3**) and (**4**)† were prepared by treating dimedone with but-3-enol and pent-4-enol in 79 and 84% yields, respectively. Irradiation of a 0·5% cyclohexane solution of (**3**) and (**4**) with a 300 W high-pressure mercury lamp through a Pyrex filter afforded the single products (**5a**) and (**6a**) in 50—60% yields. In a typical experiment using 4 g of (**3**), the starting material completely disappeared after 6 h of irradiation. The reaction mixture was concentrated and chromatographed over alumina using light petroleum–ether (1 : 1) as solvent to give a colourless oil (**5a**).



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† All new compounds afforded satisfactory elemental analyses and spectroscopic data. Complete spectroscopic and degradative details will be given in a full paper.

Although spectral data indicated the two possible structures (**5a**) and (**5b**) for (**5**), and (**6a**) and (**6b**) for (**6**), chemical evidence excluded the structures (**5b**) and (**6b**). Upon treatment with BF_3–Et_2O at room temperature (**5a**) and (**6a**) readily isomerized to the dihydrofuran (**7**), m.p. 49·5—50°, and the dihydropyran (**8**), m.p. 40·5°, respectively. No olefinic proton resonances were observed in the n.m.r. spectra of (**7**) and (**8**), thus supporting the structures assigned. The structure of (**7**) was further confirmed by chemical transformation. Warming an aqueous solution of (**5a**) or (**7**) afforded the same product (**9**), m.p. 67—68°, which, upon treatment with acetic anhydride and pyridine, gave the diketo-acetate (**10**), m.p. 35—36°, and, upon treatment with BF_3–Et_2O, gave (**7**). Attempts to epimerize either (**5a**) or (**6a**) with sodium methoxide were unsuccessful, suggesting that these photoproducts are thermodynamically stable.

The direction of the cycloaddition found in the previous[2] and present studies is in good agreement with the known tendency[1] observed in the intramolecular photocycloaddition reactions of non-conjugated dienes. Another feature of the photocycloaddition of (**1b**), (**3**), and (**4**) is the stereospecific formation of (**2b**), (**5a**), and (**6a**). One explanation for this involves a photochemically allowed $[_{\pi}2_a + _{\pi}2_a]$ process for (**1b**) and a $[_{\pi}2_s + _{\pi}2_s]$ process for (**3**) and (**4**).[3] The preliminary results, however, imply that these photoreactions proceed *via* a stepwise process involving biradical intermediates.

(*Received*, *4th December* 1972; *Com.* 2013.)

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[1] *E.g.* W. L. Dilling, *Chem. Rev.*, 1966, **66**, 373; R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, 1967, **89**, 4932; J. R. Scheffer and B. A. Boire, *Tetrahedron Letters*, 1970, 4741.

[2] Y. Tamura, Y. Kita, H. Ishibashi, and M. Ikeda, *Chem. Comm.*, 1971, 1167; *Tetrahedron Letters*, 1972, 1977.

[3] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.