

Wavelength Effect on the Competitive Photoisomerizations of 2,6-Dimethylhepta-1,3,5-triene

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Summary When irradiated at 254 nm the *Z*-hexatriene (2) gives mainly the *E*-isomer (3), whereas at wavelengths > 280 nm, the main photoprocesses are internal cycloadditions and hydrogen migration.

In the course of our study¹ of the correlation of the ground-state conformations of polyenic compounds with their photochemical reactivities,² we have observed a dramatic wavelength dependence of the photoisomerization of 2,6-dimethylhepta-1,3(*Z*),5-triene (2), obtained by the concerted photochemical ring opening of 1,5,5-trimethylcyclohexa-1,3-diene (1).³ Its photochemical behaviour is largely different from that of its 4-methylated analogue.⁴

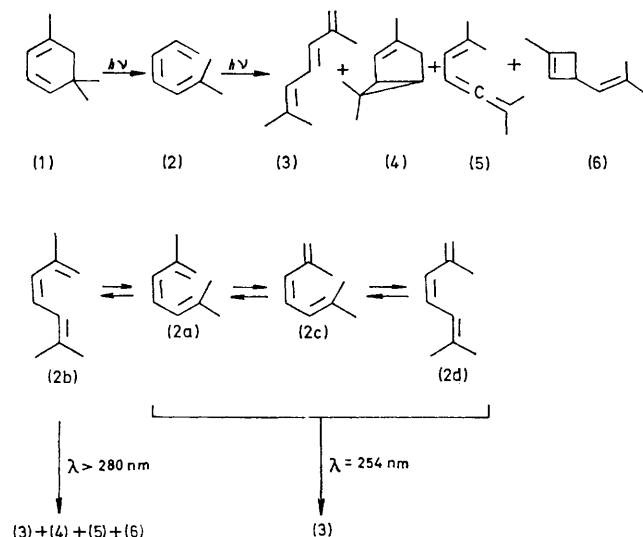
When irradiated at $\lambda > 280$ nm (Hanau medium-pressure mercury arc TQ 150; Duran filter), the *Z*-dimethylhepta-triene (2) [λ_{\max} (EtOH) 283(sh), 273, and 264 nm] undergoes several competitive photoprocesses which lead to a mixture of the following photoproducts:† the 2,6-dimethylhepta-1,3(*E*),5-triene (3)⁵ [λ_{\max} = (EtOH) 283, 272, and 262 nm] formed by *cis-trans*-photoisomerization of (2) (the photoequilibrium between these isomers is largely in favour of the *E*-triene); the 3,6,6-trimethylbicyclo[3,1,0]-hex-2-ene (4) formed by a [$4_{\pi} + 2_{\pi}$] internal cycloaddition²; the ene-allene isomer (5) originating from (2) by a [1,5] sigmatropic hydrogen shift. This reaction is thermally reversible and yields quantitatively the original *Z*-triene (2) in 20 min at 118 °C; the fourth product (6) is a vinylcyclobutene formed by [$2_{\pi} + 2_{\pi}$] internal cycloaddition and it may originate from any of the *Z*- and *E*-trienes. A stereospecific concerted thermal cycloreversion (20 h at 80 °C) yields quantitatively the *E*-triene (3) by a conrotatory process.

When the trienes (2) and (3) have disappeared completely, the photoproducts (4)–(6) are in the proportion 38:41:21.

† Analytical and preparative separations were performed by g.l.c. using 20% carbowax 20 M at 80 °C, 20% XF 1150 at 75 °C, or 20% and 30% SE30 at 80 °C. (Identification by u.v. and n.m.r. spectroscopy).

‡ The irradiations were performed at room temperature but the products have the same distribution upon irradiation at –20 °C at $\lambda > 280$ nm.

If the irradiation of the *Z*-triene (2) is performed at 254 nm (Hanau low-pressure mercury arc, TNN 15/32), *cis-trans*-isomerization is strongly favoured yielding a high proportion of the *E*-triene (3) (> 70%) and the other competitive photoprocesses are largely inhibited: only 10% of bicyclo[3,1,0]hexene (4) and of ene-allene (5) could be detected. If the irradiation is continued, the *Z*- and *E*-trienes are decomposed but the proportions of photoisomers (4) and (5) remain small.



This wavelength effect‡ on the photochemical behaviour of the *Z*-triene (2) is probably conformational in origin, but this does not imply that the influence of the ground-state

equilibrium predominates; conformations having a lower barrier, even if in relatively small proportions, may play an important role, according to the Curtin-Hammett principle.⁶

Our present interpretation is the following: at longer wavelengths, conformation (2b) (the only one having the correct geometry) of the *Z*-triene would be preferentially

excited, leading to internal cycloaddition and hydrogen-shift reactions, whereas at shorter wavelengths, the other conformations and more probably (2d) would lead to *cis-trans*-isomerization processes.

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¹ For preceding paper in the field: 'Correlation between ground-state geometry and photochemical processes,' see ref. 4.

² P. Courtot, 'Isomérisations photochimiques de polyènes conjugués,' in P. Courtot, 'Eléments de photochimie avancée,' ed., Hermann, Paris, 1972, p. 187.

³ Prepared from isophorone according to the procedure given by W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, 1967, **89**, 5734.

⁴ P. Courtot, R. Rumin, and J. Mahuteau-Corvest, *Tetrahedron Letters*, 1973, 899.

⁵ T. S. Sorensen, *Canad. J. Chem.*, 1964, **42**, 2781.

⁶ E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 151, 237.