Photoisomerizations of Cyclohexadienes and Hexatrienes. Stereochemistry and Role of Multiplicity of the Excited State

By Pierre Courtot* and Jean Yves Salaün

(*Laboratoire de Photochimie Organique, Université de Bretagne Occidentale*, 6, *Avenue le Gorgeu*, 29283 *Brest*, *France*)

Summary 5-Phenylhepta-1,3*Z*,5*E*-triene, the sole product obtained from irradiation of 6-methyl-1-phenylcyclohexa-1,3-diene, is photoisomerized to the (3*Z*,5*Z*)-triene by direct irradiation and to the (3*E*,5*E*)- and (3*E*,5*Z*)-trienes by triplet excitation; 2-methyl-6-phenylocta-2,4*Z*,6*E*-triene, obtained from 5,5,6-trimethyl-1-phenylcyclohexa-1,3-diene, behaves similarly.

The stereospecific conrotatory photochemical ring opening of cyclohexa-1,3-diene derivatives to hexa-1,3,5-trienes is now well documented,[1,2] but the predominance of one conformation of the cyclic diene may favour one of the two allowed conrotatory modes.[1,3] In the cyclohexa-1,3-dienes (**1**) and (**2**) which we have studied, the preferred half-chair conformation contains the C-6 methyl group in a pseudo-axial position.

We have shown that the photochemical ring opening of these dienes gave in each case a single photoisomer, to which the (*Z*,*E*) configuration† was assigned. The formation of a single primary photoproduct in this reaction can be explained by application of the least-motion principle;[4] starting from a methyl group in a pseudo-axial position on

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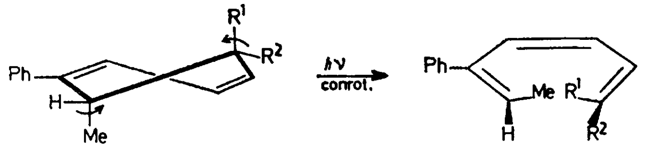
† Throughout this communication, *E* and *Z* designations are cited in numerical sequence.

the cyclohexadiene ring, rotation to the 'internal' side of the triene is much easier than to the 'external' side, the opposite being true for a pseudo-equatorial situation.



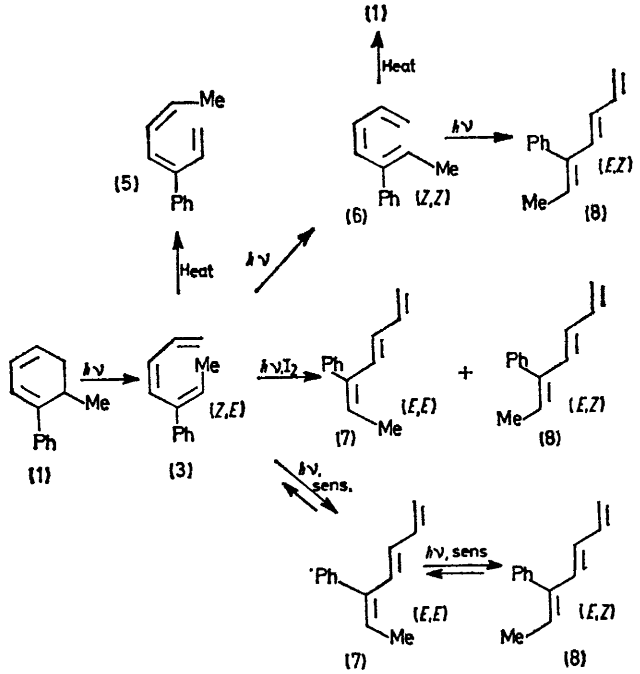
(1) $R^1=R^2=H$
(2) $R^1=R^2=Me$
(3) $R^1=R^2=H$
(4) $R^1=R^2=Me$

The primary photoproducts, the heptatriene (**3**) and octatriene (**4**), were assigned the (*Z*,*E*) configurations from their abnormal u.v. absorptions (235 and 245 nm, respectively), caused by steric interaction in the delocalized system[5] and from the easy thermal isomerization of (**3**) to (**5**) by a [1,7] hydrogen shift, which is characteristic of an (*E*) configuration of the terminal double bond.

TABLE

Sensitizer	Triplet energy/ kcal mol^{-1}	Photostationary state (%) (3)	(6)	(7)	(8)
Benzophenone	69	50	5	25	20
Michler's ketone	61	50	5	25	20
Fluorenone	53	80	4	10	6

The further photoisomerization of the triene (**3**) was of interest, because there may be different rates for the central and terminal double bonds, according to the multiplicity of the excited state involved. By direct excitation (singlet) the (*Z*,*E*)-triene (**3**) is more easily isomerized around the terminal double bond, yielding a (*Z*,*Z*)-triene (**6**) which is further photoisomerized into an (*E*,*Z*)-triene (**8**). Iodine-catalysed photoisomerization of triene (**3**) yields a mixture of the (*E*,*E*)-triene (**7**) (30%) and the (*E*,*Z*)-triene (**8**) (70%). Sensitization experiments show a different course; the position of photostationary equilibrium for any of the trienes (**3**), (**6**), (**7**), and (**8**) depends on the sensitizer (Table). The (*Z*)-central triene (**3**) always predominates, in contrast to the results for direct excitation. It is remarkable that the use of fluorenone as a sensitizer causes the formation of 80% of the (*Z*,*E*)-triene (**3**) from any of the other trienes (**6**), (**7**), and (**8**).



Our results confirm theoretical predictions[6] that a singlet reaction should cause preferential photoisomerization of the terminal double bond of a hexatriene, while a triplet reaction should lead to a more rapid isomerization around the central double bond.

The thermal behaviour of these trienes is in accordance with their configurations; the triene (**6**) cyclises easily into (**1**) (with no H-shift) whereas (**7**) and (**8**) are thermally stable owing to their central (*E*)-configuration.

(*Received, 2nd December* 1975; *Com.* **1343**.)

[1] P. Courtot and R. Rumin, *Bull. Soc. chim. France*, 1969, 3665.
[2] P. Courtot and R. Rumin, *Bull. Soc. chim. France*, 1972, 4238.
[3] J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 6444.
[4] O. Rice and E. Teller, *J. Chem. Phys.*, 1938, **6**, 499.
[5] T. S. Sorensen, *Canad. J. Chem.*, 1964, **42**, 2781; P. Courtot, R. Rumin, and J. Mahuteau, *Tetrahedron Letters*, 1973, 899.
[6] N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, 1971, **93**, 4427; H. E. Simmons, *Progr. Phys. Org. Chem.*, 1970, **7**, 1.