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The Role of Steric Factors in the Photochemistry of Substituted Cyclohexa-1,3-dienes

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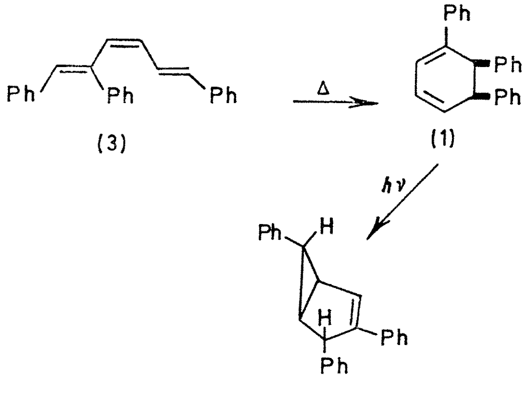
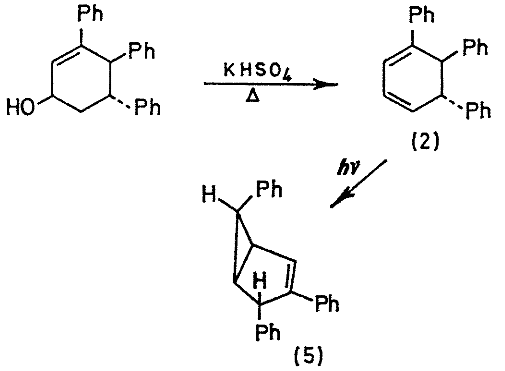
Summary Irradiation of *cis*-1,5,6-triphenylcyclohexa-1,3-diene gave *exo,exo*-3,4,6-triphenylbicyclo[3,1,0]hex-2-ene whereas irradiation of the corresponding *trans*-cyclohexadiene gave the 4-*exo*,6-*endo*-substituted bicyclohexene; secondary steric factors appear to control the direction of the conrotatory ring opening.

THE photochemical isomerization of variously substituted cyclohexa-1,3-dienes to the corresponding-1,3,5-triene is well established and has been found to proceed stereospecifically.[1] The geometry of the product can be predicted from orbital symmetry considerations.[2] The formation of bicyclo[3,1,0]hexenes on irradiation of cyclohexadienes represents another general reaction of this system.[3] The available evidence indicates that the immediate precursor of the bicyclo[3,1,0]hex-2-ene is the initially formed hexa-1,3,5-triene[4] which undergoes further symmetry-allowed photocyclization *via* a $\pi^4s + \pi^2a$ route.[5] The influence of substituents on the preferred course of the reaction and the factors controlling their stereochemistry have not been thoroughly elucidated. In an attempt to evaluate the steric factors of substituents in the bond reorganization of cyclohexa-1,3-dienes, we have examined the photochemistry of *cis*- and *trans*-1,5,6-triphenylcyclohexadiene, (**1**) and (**2**).

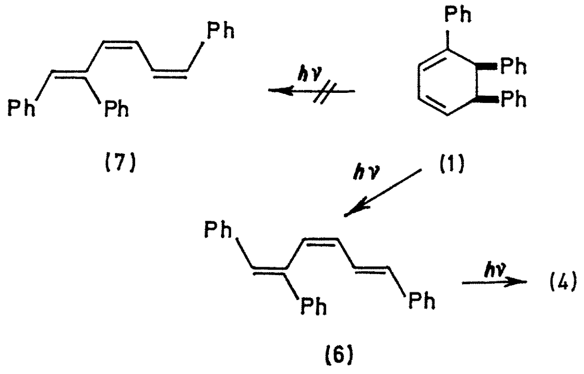


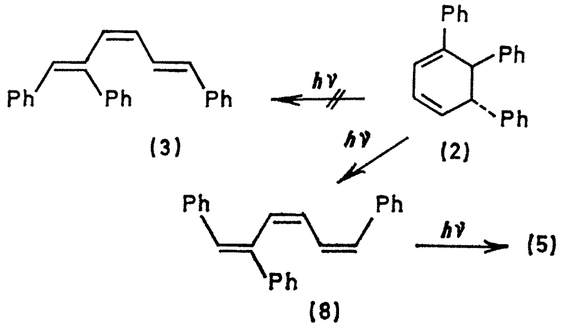


cis-1,5,6-Triphenylcyclohexa-1,3-diene (**1**) [m.p. 108—109°; n.m.r. (CDCl$_3$) δ 3·91 (1H, d, J 8·7 Hz), 4·45 (1H, m), 5·9 and 6·3 (2H, m), and 6·7—7·5 (15H, m); u.v. λ_{max} (95% EtOH) 372 (ϵ 1500), 316 (13,000), 233 (13,000) nm] was prepared by the thermal isomerization of 1,2,6-triphenyl-(*Z,Z,E*)-hexa-1,3,5-triene[5] (**3**). Irradiation of (**1**) in cyclohexane at 25° (Hanovia 450 W lamp with a Pyrex filter) gave *exo,exo*-3,4,6-triphenylbicyclo[3,1,0]hex-2-ene (**4**)[5] in high yield (71%). No other stereoisomeric bicyclohexenes could be detected by n.m.r. spectroscopy.

trans-1,5,6-Triphenylcyclohexa-1,3-diene (**2**) [clear oil; n.m.r. (CDCl$_3$) multiplets at δ 3·58, 4·04, 5·80, 6·19, 6·80, and 7·10; u.v. λ_{max} (95% ethanol) 308 (ϵ 13,000) and 233 nm (15,000)] prepared by the dehydration of *trans*-3,4,5-triphenylcyclohex-2-en-1-ol, upon irradiation rearranges stereospecifically to give 4-*exo*,6-*endo*-3,4,6-triphenylbicyclo-[3,1,0]hex-2-ene (**5**) in good yield (65%). Again, no other stereoisomeric bicyclohexenes could be detected by n.m.r. spectroscopy.

The exclusive formation of (**4**) from the irradiation of (**1**) probably follows a photochemically induced electrocyclic ring opening of (**1**) to 1,2,6-triphenyl-(*E*,*Z*,*E*)-hexa-1,3,5-triene (**6**) followed by subsequent closure to (**4**). In fact, in the partial photolysis of (**1**), the presence of (**6**) could be detected by n.m.r. spectroscopy. We have previously shown that (**6**) rearranges to (**4**) on irradiation.[5] The isomeric *Z*,*Z*,*Z*-hexatriene (**7**), if formed would have cyclized to (**5**).[5] Two modes of conrotatory motion are possible in the ring opening of (**1**). The results indicate that the process leading to (**6**) is followed exclusively. We attribute this high degree of stereospecificity to secondary forces operative during the bond reorganization step. Thus, as bond rotation in (**1**) commences toward triene (**7**), two phenyl groups are brought into a *cis*-stilbene relationship. The steric factors generated in this manoeuvre are apparently sufficient to raise the activation to a level which permits operation of the alternate rotation which leads to triene (**6**) (*trans*-stilbene relation).





Similarly, two modes of conrotatory motion in (**2**) are possible; movement in one direction leads to (**8**) while movement in the other direction will give (**3**). Triene (**8**) has been shown to cyclize to (**5**) whereas (**3**) gives (**4**) on irradiation.[5] Again it appears as though secondary steric factors control the bond reorganization of *trans*-cyclohexadiene (**2**).

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[4] Ullman and his co-workers have claimed however, that certain cyclohexadienes can be photochemically transformed to bicyclo-[3,1,0]hex-2-enes without the intermediacy of hexa-1,3,5-trienes, see E. F. Ullman, W. A. Henderson, and K. R. Huffman, *Tetrahedron Letters*, 1967, 935.

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