Tetrahedron Letters No. 24, pp 2061 - 2064, 1976. Pergamon Press. Printed in Great Britain.

NEW STRONG EVIDENCE IN FAVOUR OF A STEREOSPECIFIC $\{\pi^4a + \pi^2a\}$ PHOTO-DIELS-ALDER REACTION OF ACYCLIC HEXATRIENES.

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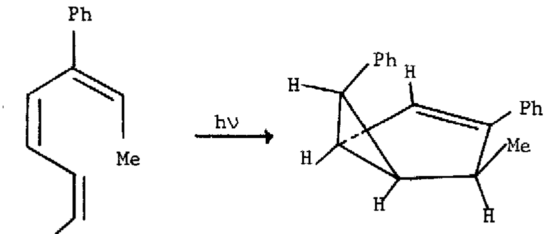
(Received in UK 21 April 1976; accepted for publication 3 May 1976)

The discussion is still open concerning the steric course of hexatriene to bicyclo {3.1.0} hexene, a so called photochemical DIELS-ALDER reaction. The theoretical treatment of this process is not yet well established (1,2), but we bring new and strong experimental evidence for a $\{\pi^4a + \pi^2a\}$ stereospecific course in the case of three acyclic hexatrienes free from geometric constraints. We have synthetized all of the eight possible geometric isomers of 1,5-diphenyl-1,3,5-heptatriene in order to authenticate the structural assignments and to be able to monitor unambiguously the photochemical reaction by NMR.

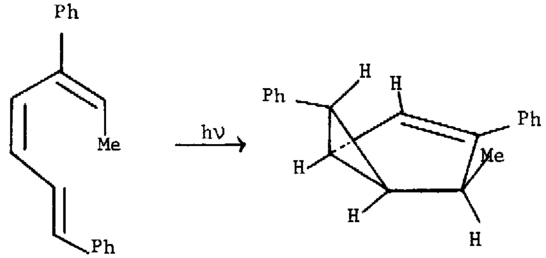
This intramolecular DIELS-ALDER photocycloaddition has in most cases been observed on hexatrienes issuing from the photochemical ring opening of cyclohexa-1,3-dienes and the stereochemistry of the intermediate hexatriènes could not be established without ambiguity : DAUBEN et al. proposed a $\{\pi^4a + \pi^2a\}$ route in the cases of cycloundeca-1,3,5-trienes (3) but SEELEY, and SCHMID et al. (4) favoured a non-concerted mode. On the other hand PADWA et al. (5) deduced a $\{\pi^4s + \pi^2a\}$ cyclization mode, starting from two 1,2,6-triphenyl-1,3,5-hexatrienes, which are supposed to undergo a preliminary *cis-trans* photoisomerization. So it was important to work with compounds with firmly established configurations and free of strong steric interactions (acyclic).

The eight stereoisomers of 1,5-diphenyl-1,3,5-heptatriene were prepared by conrotatory photochemical ring opening of the corresponding *cis* and *trans* 1,5-diphenyl-6-methyl cyclohexa-1,3-dienes and by WITTIG synthesis. Their structures were unambiguously assigned by chemical and spectral arguments (6). The four trienes with a central *cis* double bond (1 to 4) were photolyzed, and the reaction was monitored by NMR spectroscopy. In addition to *cis-trans* photoisomerization reactions of the trienes, we observed at the beginning of the reaction, the formation of a bicyclo {3.1.0} hexene derivative as a primary product (except in the case of 4), and in some cases a second bicyclic photoisomer was formed from a previously photoisomerized hexatriene. In a typical experiment, a 2.5 x 10^{-3}M pentane solution of E,Z,Z-triene 3 was irradiated under nitrogen using a high pressure mercury arc (HPK 125 W) through a "Pyrex" filter : after 5 min. 7% of bicyclohexene 7 was formed (and no other bicyclic isomer), as 40% of the initial triene had isomerized (to 24% of 2 and 5% and 4% of E,E,Z and E,E,E trienes respectively); after 10 min. 13% of 7 was formed (and no other bicyclic compounds) and 60% of the initial triene had reacted; it was only after 15 min. of irradiation that 3% of the bicyclohexene 6 was formed, evidently from the E,Z,E-triene 2, present to 28% in the mixture.



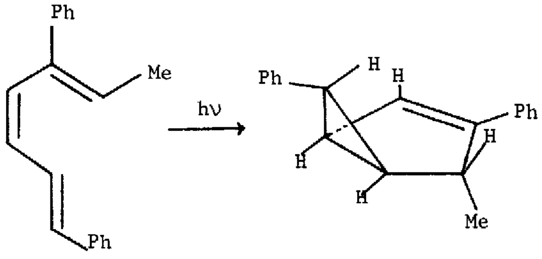
+ *cis-trans* photoisomerized trienes

1 Z,Z,E 5 *endo-endo*



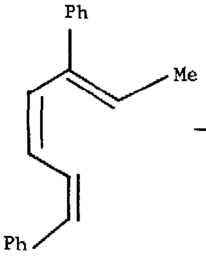
+ *cis-trans* photoisomerized trienes

2 E,Z,E 6 *endo-exo*



+ *cis-trans* photoisomerized trienes

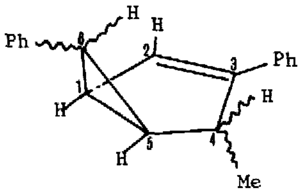
3 E,Z,Z 7 *exo-exo*



$\xrightarrow{h\nu}$ only *cis-trans* photoisomerized trienes

4 Z,Z,Z

Structures of the three bicyclohexenes 5, 6 and 7 were determined from their NMR spectra, and especially from the values of the $J_{1,6}$, $J_{5,6}$ and $J_{4,5}$ coupling constants : it is known that *cis*-vicinal coupling in a cyclopropane is higher than *trans*-vicinal coupling (6.9 to 9.3 Hz for J_{cis} compared to 2.6 to 5.6 Hz for J_{trans}). There is also a correlation between $J_{4,5}$ and the *exo* or *endo* situation of H_4 : $J_{4,5} \sim 0$ when H_4 *endo*(near 90° dihedral angle in 7) and $J_{4,5} \sim 7$ Hz when H_4 *exo* (near 0° in 5 and 6). These coupling constants were measured on a BRUKER 90 MHz spectrometer and the spectra were simulated when the constants could not be determined directly (7). The H_6 proton is influenced by the double bond of the cyclopentene ring(shielding when in *endo* position (1.5 δ) and deshielding when in *exo* (2.4 δ)).



	$J_{4,5}$	$J_{1,2}$	$J_{1,4}$	$J_{2,4}$	$J_{1,5}$	$J_{5,6}$	$J_{1,6}$
5	7	2	< 1	2	6	-	-
6	7	2	< 1	1,5	-	-	-
7	< 1	2	3	1,5	6	3	3

The particular stereospecificity of these photocycloadditions is intriguing : a concerted allowed mode in the excited state would be predicted as $\{\pi^4 s + \pi^2 a\}$ or $\{\pi^4 a + \pi^2 s\}$ (1). In none of the three examples described here, is there any strong steric demand in the triene, which could overwhelm the orbital factors. On the contrary, an *endo-endo* configuration of the bicyclic photoisomer 5 indicates a true primary photochemical product, with no thermodynamic equilibration. We have no definitive interpretation of the particular stereospecificity of the reaction. It may be due to a distinct excitation of the butadiene and ethylene parts of the hexatriene molecule, or to a reaction from a hot ground state. It is only compatible with an orbital control, and excludes a steric influence such as the two-step procedure suggested by DAUBEN et al. (3,8) (closure to a cyclopropane ring followed by closure to the cyclopentene ring, governed by thermodynamical stability).

Aknowledgments : we thank the C.N.R.S. for a grant supporting this work in part (ATP N° 2 799 05).

References and notes

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(7) Thanks are due to Miss V. MICHON and to Dr. J.Y. LALLEMAND who measured these spectra in the Laboratoire de Chimie, Ecole Normale Supérieure, Paris.

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