

## Quenching of the Excited Singlet Penta-1,3-dienes by $\text{Me}_3\text{SnH}$ : Evidence against the Allylmethylene Configuration of the Relaxed $S_1$ State

By MICHAEL BIGWOOD and STÉPHANE BOUÉ\*

(Department of Organic Chemistry, Physical-Organic Chemistry Grouping, Free University of Brussels, 50 F. D. Roosevelt Ave., 1050 Brussels, Belgium)

**Summary** The 1,4 concerted addition of  $\text{Me}_3\text{SnH}$  to the singlet excited penta-1,3-dienes yields *cis*- and *trans*-adducts according to a stereochemistry which is incompatible with an allylmethylene relaxed configuration and suggests a doubly twisted state.

Much work has been devoted during the past few years to the properties of electronically excited singlet conjugated dienes and yet the structure and the decay mode(s) of this state are not clearly established.<sup>1</sup> Theoretical predictions<sup>2</sup> favour relaxation by the 90° twist of one  $p_\pi$  orbital leading to an allylmethylene configuration. A study on the penta-1,3-dienes<sup>3</sup> has unambiguously demonstrated that the  $S_1$  state can neither be twisted at both ends of the  $\pi$ -system nor undergo a rapid interconversion by successive rotations of the orbitals at C(1) and C(4) as observed for the triplet state.<sup>4</sup> Saltiel has however shown in the case of the hexa-

2,4-dienes<sup>5</sup> that rotation at one end of the  $\pi$ -system does occur efficiently, which is compatible with the allylmethylene also proposed by Dauben.<sup>6</sup> We have already mentioned<sup>7</sup> that the experimental data might as well or even better be accounted for by a partial 1,3-overlap of  $p_\pi$  orbitals resulting in a doubly twisted [about C(1)-C(2) and C(2)-C(3)] entity. We report here on the quenching of the  $S_1$  penta-1,3-dienes by  $\text{Me}_3\text{SnH}$ , whose results cannot be accommodated by the allylmethylene hypothesis and reinforce the model based on the 1,3 interaction.

Apart from 3-methylcyclobutene (I) and geometrical isomers which are the normal photoproducts in solution, the excitation at 253.7 nm of penta-1,3-dienes mixed with  $\text{Me}_3\text{SnH}$  (molar ratio 1:3) yielded the two adducts (II) and (III) as the major products;† the appearance of the adducts obeys a linear kinetic plot with a zero intercept and the mixture composition did not change once the light was

† Satisfactory mass and n.m.r. spectra were obtained.

turned off, thus evidencing that (II) and (III) are primary products stable to the experimental conditions. The quantum yields for these reactions are given in the Table.

In spite of the high concentration in hydride which renders possible a static quenching,  $\Phi$  (cyclobutene) is not decreased<sup>3</sup> which indicates that the *s-cis* excited singlet is extremely short-lived and probably decays exclusively $\ddagger$  to (I) within the time required to rotate concertedly the  $p_\pi$  orbitals at C(1) and C(4). The relaxation to the allyl-methylene structure is hence ruled out for the *s-cis* conformers.

TABLE. Quantum yields for the products formed by irradiating the penta-1,3-dienes in the presence of  $\text{Me}_3\text{SnH}$ .<sup>a</sup>

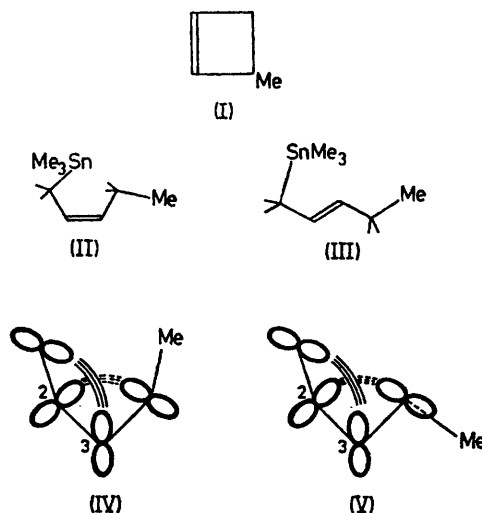
Molar composition of the starting mixture	Products				geometrical isomer
	(I)	(II)	(III)	(III)	
<i>trans</i> -Penta-1,3-diene:					
$\text{Me}_3\text{SnH}$ (1:3), neat	..	0.03	0.10	0.50	ca. 0
<i>cis</i> -Penta-1,3-diene:					
$\text{Me}_3\text{SnH}$ (1:3), neat	..	0.003	0.20	0.25	0.15

<sup>a</sup> Measured on oxygen-free solutions in sealed quartz tube at diene conversions ranging from 20–60%; light intensity:  $3.2 \times 10^{16}$  quanta  $\text{s}^{-1}$  at 253.7 nm (there is no absorption by the hydride under these conditions).

Our results are in marked contrast to those for radical (thermal) addition where a major product from each diene is the 1,2-adduct in which the configuration of the 3,4-double bond is retained<sup>8</sup> and where the *cis*-diene only undergoes a stereospecific 1,4-addition yielding (III); thus the photochemical reaction features (i) the total absence of any 1,2 adduct, (ii) a stereoselectivity displayed by the *trans*-diene only, and (iii) a stereochemical course different from that obtained in the thermal addition.<sup>8</sup> These data imply that the 1,4-addition to the  $S_1$  diene be concerted, for in a two-step process the abstraction of a hydrogen atom from the hydride would produce a ground state allyl radical from which the 1,2 adducts should arise as well as in the thermal reaction.

Considering that most of the diene molecules lie as *s-trans* conformers when excited, the relaxation to a frozen $\S$  allylmethylene species would not be consistent with the production of a large amount of the *cis*-adduct and even worse with the higher yield of the latter originating from the sterically congested *cis*-penta-1,3-diene. It is clear that the actual structure of the relaxed  $S_1$  state of dienes must basically fulfil the requirements imposed by the formation of a *cis*-C(2)–C(3) double bond, *i.e.* the  $\pi$ -orbitals at C(2) and C(3) must be almost orthogonal in terms of energy. As the  $\pi$  system must also be twisted at one of its ends,<sup>6</sup> it appears

evident that the excited singlet makes use of two concerted 1,3- $p_\pi$  bonding interactions to dive into an energy well and acquire the doubly twisted configuration (IV) or (V) (respectively from the *cis* or the *trans*-penta-1,3-dienes) which in fact represent some kind of intermediates along the  $S_1$  reaction co-ordinate from a diene to the corresponding bicyclobutane. $\P$



The concerted 1,4 addition of  $\text{Me}_3\text{SnH}$  to (IV) or (V) can proceed by either an inward or an outward motion of C(1) and C(4) [with respect to the C(2)–C(3) bond] leading respectively to the *cis*- or to the *trans*-adduct. According to our model the relaxed  $S_1$  state bears a quasi-*endo* methyl in (IV) and a quasi-*exo* methyl in (V); therefore the difference in addition stereoselectivity, displayed by the two isomeric dienes, becomes understandable since a frontal approach of the hydride preferred with (V) may favour the *trans*-adduct whereas a side-attack sterically induced by the *endo*-methyl in (IV) may force to some extent the *cis*-bonding. A mechanism of this type, which probably involves a reversible complex,<sup>7b</sup> also accounts for the effect of  $\text{Me}_3\text{SnH}$  on the quantum yields of geometrical isomerization:  $\Phi$  (*cis*)  $\rightarrow$  (*trans*) is enhanced up to 0.15, *i.e.* more than 30% of the molecules decaying to the ground state dienes, whereas  $\Phi$  (*trans*)  $\rightarrow$  (*cis*) drops to *ca.* zero (*vs.* 0.10 and 0.08 in dilute cyclohexane solution).

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$\ddagger$  This assumption is based on the experimental observation that  $\Phi$  (cyclobutene)  $\sim$  % *s-cis*,<sup>9</sup> but is subject to the condition that the extinction coefficients are the same for the *s-cis*- and *s-trans*-conformers.

$\S$  A freely rotating allyl moiety cannot be invoked as the isomerization quantum yields for the penta-1,3-dienes do not exceed 10%<sup>3</sup>

$\P$  Until reaching the point of lowest energy this co-ordinate may well be common for the bicyclobutane and for the methylene-cyclopropyl diradical from which cyclopropenes originate.<sup>7</sup>

<sup>1</sup> For a review, see J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafriou, *Org. Photochem.*, 1973, 3, 1.

<sup>2</sup> E. M. Evleth, *Chem. Phys. Letters*, 1969, 3, 122; N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, 1971, 93, 4427; K. Inuzuka and R. S. Becker, *Bull. Chem. Soc. Japan*, 1971, 44, 3323.

<sup>3</sup> S. Boué and R. Srinivasan, *J. Amer. Chem. Soc.*, 1970, 92, 3226.

<sup>4</sup> H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1969, 91, 2852.

<sup>5</sup> J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, 1970, 92, 3227.

<sup>6</sup> W. G. Dauben and J. S. Ritschers, *J. Amer. Chem. Soc.*, 1970, 92, 2925.

<sup>7</sup> (a) R. Srinivasan and S. Boué, *Angew. Chem. Internat. Edn.*, 1972, 11, 320; (b) M. Bigwood and S. Boué, *Tetrahedron Letters*, 1973, 4311.

<sup>8</sup> H. J. Albert, W. P. Neumann, W. Kaiser, and H. P. Ritter, *Chem. Ber.*, 1970, 103, 1372.

<sup>9</sup> L. M. Sverdlov and E. N. Bolotina, *Russ. J. Phys. Chem.*, 1962, 36, 1502.