Divergent Stereochemistry of Photocyclization from Singlet and Triplet States of 2-Vinylbiphenyls. *X*-Ray Crystal Structure of *cis*-9-Phenyl-10-methyl-9,10-dihydrophenanthrene

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Summary The singlet cyclization of Z(or E)-1-biphenyl-2-yl-1-phenylpropene proceeds stereoselectively to *cis* (or *trans*)-9-phenyl-10-methyl-9,10-dihydrophenanthrene (the *cis*-isomer has been characterized by *X*-ray crystallography) while the triplet cyclization gives a [*trans*]/[*cis*] ratio of 9:1 whatever the starting isomer.

Recently we have reported that, from the singlet state, 4-styrylfluorene (**1**) cyclizes more quickly than 2-styrylbiphenyl (**2**) whereas from the triplet state only (**2**) reacts. The fact that, apparently, a different geometry was required for the cyclization according to the multiplicity of the excited state, was tentatively explained by the occurrence of two mechanisms: a concerted singlet cyclization by a quasi-planar transition state and a triplet pathway involving a twisted methylene double bond.[1,2] In order to substantiate or disprove this proposal we have now established the stereochemistry of this reaction from both excited states.‡

For this purpose we have prepared 1-biphenyl-2-yl-1-phenylpropene (**3**)§ by dehydration of the benzylic alcohol with $SOCl_2$–pyridine;¶ the two isomers are formed in a Z:E ratio of 75:25. The configurations were unambiguously assigned by a ^{13}C n.m.r. analysis.[5] In the ^{1}H n.m.r. spectrum, the Z isomer shows the ethylenic proton resonance, *cis* to the phenyl group, at lower field (δ 5·95 *vs.* 5·75) and

Table. Irradiation of 1-biphenyl-2-yl-1-phenylpropene (**3**).

	Reactants[b]		Products[b]	
Sensitizer	E-:Z-(**3**)/%	Conversion/%	E-:Z-(**3**)/%	*trans*-:*cis*-(**4**)/%
None[a]	96·5:3·5	4	95:5	96:4
		83	64:36	71:29
	1:99	11	2:98	2·5:97·5
		92	26:74	8:92
Benzophenone[c]	96·5:3·5	27	95:5	10:90
		100		11:89
	1:99	10	1:99	11:89
		100		10:90
Xanthone[c]	96·5:3·5	15	95:5	10:90
		100		10·5:89·5
	1:99	9	2·5:97·5	10:90
		100		10:90

[a] Direct irradiation at 300 nm (Rayonet), in a quartz tube, of a cyclohexane solution of (**3**) (5×10^{-4} M) and piperylene (10^{-3} M). [b] Relative yields were determined by a standard g.c. technique. [c] Irradiation at 350 nm (Rayonet), in a Pyrex tube of a degassed benzene solution of (**3**) (5×10^{-4} M) and benzophenone (2×10^{-2} M) or xanthone (2×10^{-3} M).

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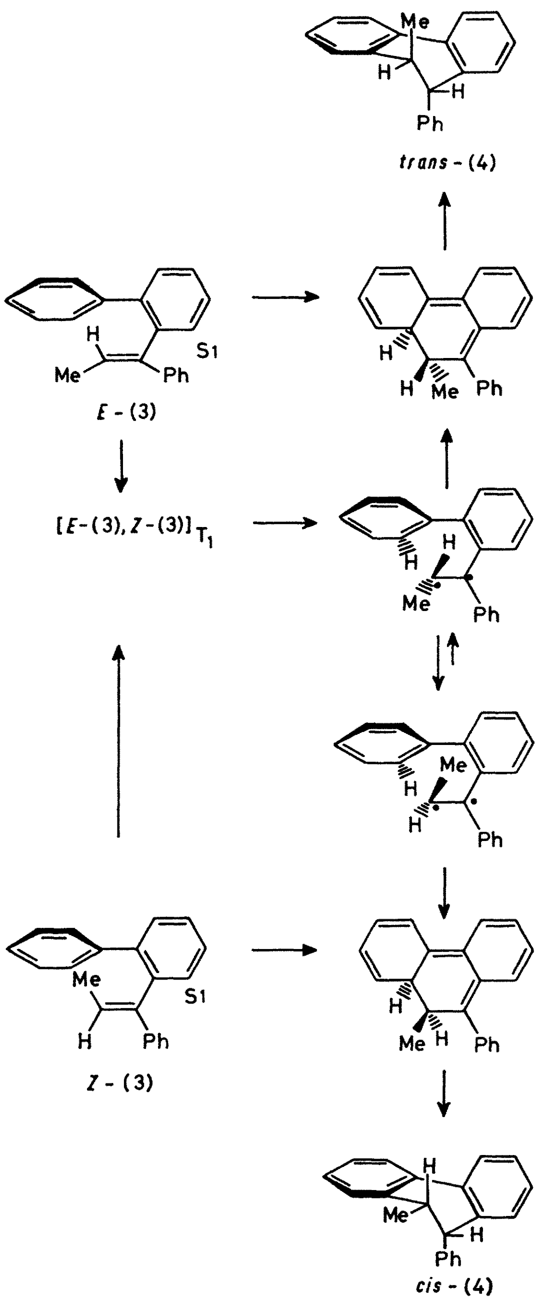
‡ Laarhoven (in ref. 3) has recently shown that, from a *trans*-β-aryl-2-vinyl biphenyl, only one isomer was formed by the singlet state: the isomer that should arise *via* a conrotatory cyclization followed by a suprafacial [1,5] sigmatropic hydrogen shift. But he did not observe this reaction from the triplet state. Fournier (ref. 4) has isolated the intermediate of the photocyclization of arylethenylfurans and shown that it is formed from a conrotatory cyclization.

§ Satisfactory spectroscopic data have been obtained for all new compounds.

¶ With acidic dehydrating agents 9-phenyl-9-ethylfluorene is also formed.

the methyl resonance at higher field (δ 1·45 *vs.* 1·80) than the *E* isomer; these proton chemical shifts are opposite to those found with 1-α-naphthyl-1-phenyl-ethylene[6] and denote the non-planarity of (**3**).

Direct irradiation (λ 300 nm) of a degassed cyclohexane solution of *E*-(**3**) (5×10^{-4}M) and piperylene (10^{-3}M) as a triplet quencher affords, at the beginning of the reaction, only one isomer of 9-phenyl-10-methyl-9,10-dihydrophenanthrene (**4**). Under the same conditions *Z*-(**3**) gives the other isomer. Since the photoisomerization $E \rightleftharpoons Z$ is competitive with the photocyclization, the stereoselectivity of the cyclization decreases quickly with the progress of the reaction.



SCHEME

In contrast, sensitized cyclization of (**3**) with benzophenone or xanthone leads to the two isomers of (**4**) in a ratio which is constant whether *E*-(**3**) or *Z*-(**3**) is the initial reactant and at any conversion stage (Table).

cis and *trans* assignment of the two products (**4**) was not possible from n.m.r. data alone. Since Harvey[7] and Laarhoven[3] observed a de-coalescence of the resonance of the substituents and a de-coalescence and a modification of the coupling constant of the benzylic protons for *cis*-9,10-disubstituted 9,10-dihydrophenanthrenes, whereas the *trans* isomers showed temperature-independent n.m.r. spectra, we measured the n.m.r. spectra of the two photoproducts from +30 to −60 °C, but have observed no significant modification with the lowering of the temperature. The coupling constants between the benzylic hydrogens are 5·9 Hz for the isomer obtained from *Z*-(**3**) and 3·5 Hz for the isomer from *E*-(**3**). The low value obtained for the second one favours a *trans* configuration[7] but to obtain an unambiguous assignment of configuration we have carried out a single-crystal *X*-ray diffraction study of the more crystalline product; it results from the cyclization of *Z*-(**3**) and has, in fact, the *cis* configuration.

Crystal data: $C_{21}H_{18}$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13{\cdot}376(1)$, $b = 6{\cdot}969(1)$, $c = 21{\cdot}818(1)$ Å, $\beta = 130{\cdot}78(1)°$, Cu-K_α radiation, automatic Nonius CAD4 diffractometer. The structure was solved by direct methods[8] and refined by block-diagonal least squares to $R = 0{\cdot}057$. The phenyl group is pseudoaxial whereas the methyl is pseudoequatorial (Figure).

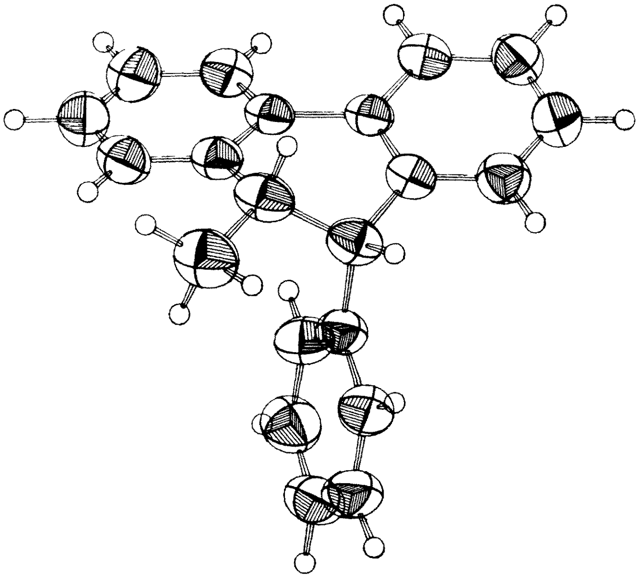


FIGURE. ORTEP drawing of *cis*-9-phenyl-10-methyl-9,10-dihydrophenanthrene (**4**).

** The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The stereoselective singlet cyclization and the non-stereoselective triplet cyclization of (**3**) provide strong support for the multiplicity-dependent mechanism we have previously proposed.[1,2] A conrotatory ring closure from the singlet state followed by a suprafacial [1,5] sigmatropic hydrogen shift accounts for the observed stereoselectivity and can now be regarded as the established mechanism of the singlet cyclization of 2-vinylbiphenyls. In marked contrast, 2-vinylbiphenyls[3,9] and polyenes in general[10] do not photocyclize, or photocyclize very inefficiently, from the triplet state. However, (**3**) is a 1,1-diarylethylene and 1-biphenyl-2-yl-1-phenylethylene[2] cyclizes efficiently from the triplet state. Since the product structure [*cis-/trans-*(**4**) = 9/1] is unchanged whatever the isomer irradiated, a common intermediate must be reached from the *E* and *Z* isomers. It could be the perpendicular triplet state; cyclization occurs from two conformers; the more favoured accommodates a hydrogen–hydrogen interaction, instead of a hydrogen–methyl, and leads to *cis*-(**4**) (Scheme).

We have prepared and irradiated, under the same conditions, the two isomers of 1-(4-fluorenyl)-1-phenylpropene: the cyclization is stereoselective from the singlet but from the triplet there is only a $Z \rightleftharpoons E$ isomerization. This result shows again the necessity of a flexible aromatic unit for the triplet cyclization and favours a cyclization from the perpendicular triplet state in the case of (**3**).

Perpendicular triplet states of stilbene[11] and styrene[12] have recently been observed directly by laser flash photolysis but their intermediacy in photoreactions, except for *cis–trans* isomerization, has not, to our knowledge, been investigated.

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