Substituent Effects in the Photocyclization of 2-Styrylbiphenyls

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Quantum yields for the photocyclization of several substituted 2-styrylbiphenyls (4) to 9,10-dihydrophenanthrenes (6) have been measured. It appears that the values fit into a linear Hammett plot and also that the substituent effects cannot be explained by ascribing them to perturbations of the orbital energies which are most involved in the photoreaction; calculations with the extended Hückel MO method did not even give qualitatively correct results always. It is supposed that substituents affect the heights and positions of the extreme in the energy curves for ground and excited state along the reaction co-ordinate. The linear plot for quantum yields *versus* σ values for the ground state suggests that the main effect is on the maximum of the energy curve for S_0.

In the preceding paper[1] we discussed the synthetic and mechanistic aspects of the photocyclization of 2-(β-arylvinyl)biphenyls into 9-aryl-9,10-dihydrophenanthrenes. In this paper we report the effect of substituents on this reaction.

For a photochemical reaction two types of effects can be expected. Substituents with considerable spin–orbit coupling (*e.g.* NO_2, Br, COR) cause a high degree of intersystem crossing (i.s.c.), thus preventing a chemical reaction from the first excited *singlet* state. This effect on the i.s.c. has been observed with stilbenes bearing such substituents.[2] They fail to undergo photocyclization.[3] Substituents with limited or no spin–orbit coupling (*e.g.* CH_3, OCH_3, F, Cl) may have an electronic (or steric) effect. This type of influence has also been demonstrated in the photocyclization of substituted stilbenes.[3,4] Jungmann *et al.*[5] found the Hammett relation (1) for the quantum yield (Φ_{cycl}) of phenanthrene formation from *meta*-substituted products when σ_p was used as the substituent constant. *para*-Substitution products did not fit a linear relationship. Mallory *et al.*[6] have also found a Hammett relation for the related photocyclization of the stilbene analogue 1,1-diphenyl-2-*p*-X-phenylethylene (1) (Scheme 1).

$$\log(\Phi_{cycl}{}^{X}/\Phi_{cycl}{}^{H}) = \rho\sigma \quad (\rho\ -1.08) \qquad (1)$$

They concluded that an energy barrier must exist for the reaction (1) $(S_1) \longrightarrow (2)$, the height of which is influenced by substituents.

In order to explain these results Güsten and Klasinč[7] have related the values of Φ_{cycl} of substituted stilbenes to the charge density on the carbon atoms involved in the cyclization. From calculations with the Hückel MO method they arrived at the conclusion that cyclization must proceed from a hot ground state. This explanation is not valid, however, as it has been firmly established that the reaction proceeds from the S_1 state of *cis*-stilbenes.[8]

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[1] P. H. G. op het Veld and W. H. Laarhoven, preceding paper.

[2] D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 3907.

[3] E. V. Blackburn and C. J. Timmons, *J. Chem. Soc.* (*C*), 1970, 172.

[4] H. Jungmann, H. Güsten, and D. Schulte-Frohlinde, *Chem. Ber.*, 1968, **101**, 2690.

[5] (*a*) H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191; (*b*) C. G. Swain and E. Lupton, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 4328.

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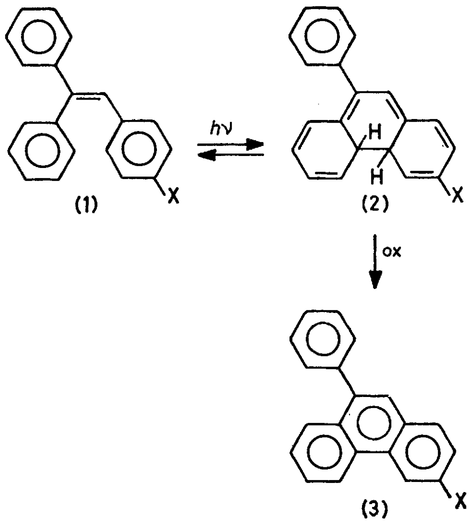
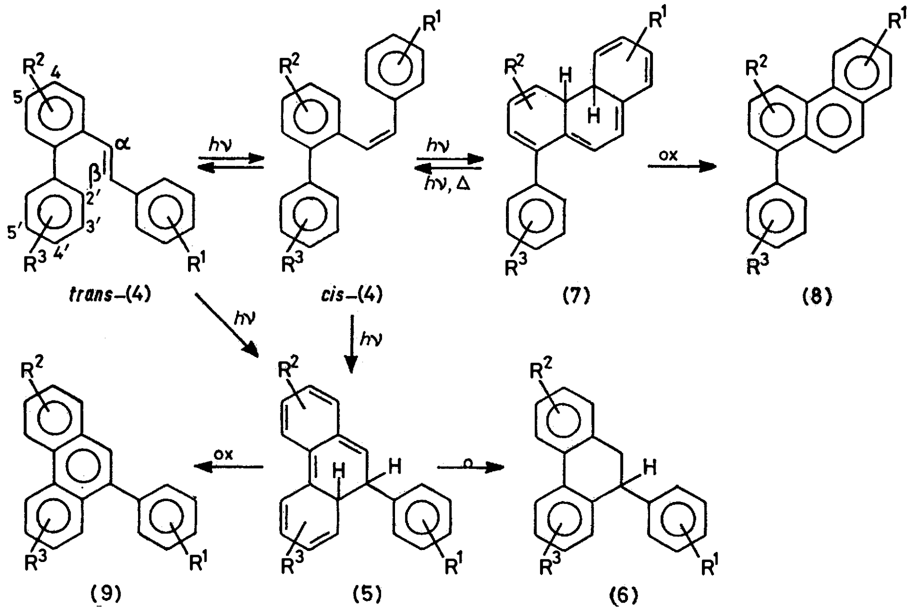
[8] (*a*) Th. Kindt, E.-P. Resewitz, Ch. Goedicke, and E. Lippert, *Z. Phys. Chem.* (*Frankfurt*), 1976, **101**, 1; (*b*) H. Stegemeyer, *Z. Naturforsch.*, 1962, **17b**, 153; (*c*) K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662; (*d*) T. J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1972, **94**, 5914; (*e*) Ch. Goedicke and H. Stegemeyer, *Chem. Phys. Letters*, 1972, **17**, 492; (*f*) R. H. Martin, *Angew. Chem.*, 1974, **86**, 727; (*g*) T. D. Doyle, W. R. Benson, and N. Filipescu, *J. Amer. Chem. Soc.*, 1976, **98**, 3263.



SCHEME 1

More recent attempts to explain the measured substituent effects on photocyclisations of stilbenes have been made by Muszkat and Schmidt[9] who calculated potential energy curves for the reversible cyclization step with the extended Hückel MO method and by Muszkat[10] who used electronic overlap populations.



(4a) R¹ = R² = R³ = H
(4b) Ph = R¹ = β—naphthyl, R² = R³ = H
(4c) R¹ = p—OCH$_3$, R² = R³ = H
(4d) R¹ = p—CH$_3$, R² = R³ = H
(4e) R¹ = p—Cl, R² = R³ = H
(4f) R¹ = p—NO$_2$, R² = R³ = H
(4g) R¹ = m—OCH$_3$, R² = R³ = H
(4h) R¹ = m—CH$_3$, R² = R³ = H
(4i) R¹ = m—Cl, R² = R³ = H
(4j) R² = 4—OCH$_3$, R¹ = R³ = H
(4k) R² = 5—OCH$_3$, R¹ = R³ = H
(4l) R³ = 3—OCH$_3$, R¹ = R² = H
(4m) R³ = 4—OCH$_3$, R¹ = R² = H

SCHEME 2

In both cases, however, only a rough, qualitative correlation with experimental results was obtained.

RESULTS

We have measured the quantum yields for the various photoreactions of several 2-(β-arylvinyl)biphenyls (4), *viz. cis–trans* and *trans–cis* isomerization, cyclization into 9-aryl-9,10-dihydrophenanthrenes (6), and cyclodehydrogenation into 1-phenylphenanthrenes (8) (Scheme 2). The results are given in Table 1. It appears that in general Φ_{ct} and Φ_{tc} are *ca.* 10 times larger than Φ_{dhp} and Φ_{phe}, which are measured for equilibrium mixtures of *cis*- and *trans*-(4).

For the quantum yield of a given reaction (Φ_R) which proceeds from the S_1 state of a molecule, relationship (2) can be deduced, in which k_R is the rate of the reaction, $\Sigma\Phi_D$ the sum of the quantum yields of all other processes that proceed from this excited state and Σk_D is the sum of the rates of these processes. Applied to the formation of (6) from (4) equation (2) becomes (3). The index X is used to indicate the substituent present in (4), k_{cycl} is the rate of the cyclization step (4) (S_1) ⟶ (5) and $\Sigma k_D{}^X$ refers to the rates of intersystem crossing, internal conversion,

$$\frac{\Phi_R}{\Sigma\Phi_D} = \frac{\Phi_R}{1 - \Phi_R} = \frac{k_R}{\Sigma k_D} \qquad (2)$$

$$\frac{\Phi_{\text{dhp}}{}^X}{1 - \Phi_{\text{dhp}}{}^X} = \frac{k_{\text{cycl}}{}^X}{\Sigma k_D{}^X} = K^X \qquad (3)$$

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[9] (*a*) K. A. Muszkat and W. Schmidt, *Helv. Chim. Acta*, 1971, **54**, 1195; (*b*) W. Schmidt, personal communication.

[10] K. A. Muszkat, personal communication.

fluorescence and, only for *cis*-(4), cyclization to (7). Equation (3) based on measured values of Φ_{dhp} is valid, because the [1,5] hydrogen shift from (5) to (6) is much faster than the cyclization of (4) (S_1) to (5). It is assumed that this sigmatropic shift is also much faster than the ring opening reaction from (5) to (4) (see ref. 1).

TABLE 1

Quantum yields for *cis–trans* and *trans–cis* isomerization (Φ_{ct} and Φ_{tc}), and for formation of 9,10-dihydrophenanthrene (Φ_{dhp}) and phenanthrene (Φ_{phe})

Compound	Φ_{ct} [a]	Φ_{tc} [a]	Φ_{dhp} [a]	Φ_{dhp} [b]	Φ_{phe} [b]
(4a)	0.29	0.46	0.023	0.021	0.013
(4b)	0.25	0.14	0.018	0.017	0.012
(4c)	0.34	0.29	0.011	0.010	<0.003
(4d)	0.32	0.48	0.016	0.015	0.003
(4e)	0.34	0.24	0.028	0.026	0.007
(4f)	0.53	0.16	<0.001	<0.001	
(4g)	0.34	0.12	0.021	0.016	0.025
(4h)	0.52	0.13	0.024	0.021	0.008
(4i)	0.29	0.74	0.053	0.046	0.011
(4j)	0.46	0.33	0.018		
(4k)	0.40	0.32	0.018		
(4l)	0.28	0.47	0.024		
(4m)	0.34	0.24	0.012		

[a] Measured at 286 nm under argon. [l]Measured at 286 nm under oxygen.

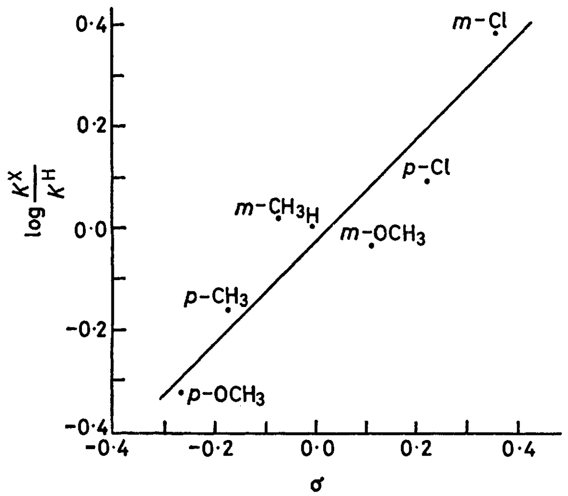

FIGURE 1 Plot of log (K^X/K^H) against Hammett δ values for compounds (4)

In Figure 1 log (K^X/K^H) for compounds (4) has been plotted against the Hammett σ values of the substituents. The straight line, calculated by the least squares method, has a slope ρ of 0.954 (r 0.92, s $>0.4\%$). This means that the probability that the linear relationship is by chance is <0.004.[11] A linear relationship with other substituent constants such as σ^+, σ^-, *etc.*,[12] appeared much less probable.

For Φ_{phe}, measured in solutions of (4) saturated with oxygen, no Hammett plot is found. This is not surprising, because the solutions contain equilibrium mixtures of *cis*- and *trans*-(4) whereas phenanthrene is only formed from *cis*-(4).

Substituent effects on Φ_{dhp} might be caused by several different factors, *e.g.* different values of Φ_{dhp} for *cis*- and *trans*-(4). It appeared, however, that nearly equal values of Φ_{dhp} were measured for solutions containing a pure *cis*- or *trans*-isomer, when the measurements were performed before the *cis–trans* equilibrium had been reached. So Φ_{dhp} cannot differ much for the *cis*- and *trans*-isomers. Moreover, no simple relation was found between *cis* : *trans* ratios in equilibrium mixtures of several compounds (4) and their Φ_{dhp} values: (4a), *c* : *t* 2.1; Φ_{dhp} 0.023; (4e), *c* : *t* 0.7, Φ_{dhp} 0.028; (4i), *c* : *t* 2.3, Φ_{dhp} 0.053. Another factor may be the cyclization of *cis*-(4) into the 4a,4b-dihydrophenanthrene (7). Quantum values for the formation of (6) in the absence or presence of oxygen show only slight differences (Table 1). In general, the values under the latter circumstances are only *ca.* 10% lower, even for those compounds for which Φ_{phe} is of the same magnitude as Φ_{dhp}.

On the basis of these considerations we conclude that the observed Hammett plot is caused by the direct influence of the substituents on the relation $k_{cycl}/\Sigma k_D$.

DISCUSSION

It is surprising that a Hammett relation is found for a reaction, which proceeds from the first excited singlet state, using substituent constants σ, which are determined for the ground state.[5] Mallory *et al.*[6] seem to have overlooked this contradiction. To gain more insight into the factors which play a role in the cyclization of 2-(β-arylvinyl)biphenyls (4) into 9-aryl-8a,9-dihydrophenanthrenes (5) we carried out extended Hückel MO calculations analogous to those of Muszkat and Schmidt.[9] These authors ascribe the substituent effects on the stilbene ⟶ 4a,4b-dihydrophenanthrene cyclization to first- and second-order perturbations of the energies of the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO), and base their explanation on the following rule. Rates and quantum yields of concerted reactions in excited states are proportional to the value of the slope of the curve of electronic energy *versus* reaction co-ordinate for the ground-state nuclear configuration of the reactant.

We have calculated the HOMO and LUMO energies and the coefficients of these orbitals for the atoms of *trans*-(4a) in this configuration, wherein the distance between C-2′ and the vinyl β-carbon is 2.70 Å.[13] The relevant values are given in Table 2.

TABLE 2

Energies and coefficients from the extended Hückel MO calculations for 2-(β-phenylvinyl)biphenyl (4a): distance C-2′–C-β 2.70 Å; energy HOMO −11.824, LUMO −8.991 eV

	Coefficients A_{ri}	
r / i	HOMO	LUMO
m	−0.065	−0.163
p	−0.248	0.379
m′	−0.043	−0.098
4	−0.114	0.150
5	−0.254	−0.139
3′	−0.031	0.029
4′	0.267	0.190
5′	0.295	0.135

Because the HOMO and LUMO are essentially π-

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[11] P. Moroney, 'Facts from Figures,' Penguin, Harmondsworth, 1957.

[12] S. L. Murov, 'Handbook of Photochemistry,' Dekker, New York, 1973.

[13] For this calculation program QCFF/PI (QCPE no. 247) was used.

orbitals, substituents can be divided in two classes. (i) First, there are substituents with π-orbitals, which conjugate with the π-electron system of (4a), with energies between those of HOMO and LUMO; *e.g.* the nitro-group has a calculated energy of -10.6 eV.[9a] Substitution of a nitro-group in any position in (4a) will thus result in a new low lying π^* orbital, which replaces the original LUMO and leads to a large first-order energy change in the LUMO. (ii) Secondly, there are substituents which contain only σ-orbitals or lone pairs in close proximity to the π-electron system, *e.g.* alkyl groups, the methoxy group, fluorine, and chlorine, with orbital energies low in comparison with the HOMO and LUMO of (4a). Therefore, the mutual perturbation is of the second-order type and can be given by equation (4). The indices i and j relate, respectively, to the

$$\delta E_i = \frac{A_{ri}^2 A_{sj}^2}{E_i - E_j}\,\beta_{rs}^2 \qquad (4)$$

parent system (4a) and the substituent, r and s the atoms in (4a) and the substituent which are bonded, E and E_j the orbital energies, A_{ri} and A_{sj} the orbital coefficients, and β_{rs} the interaction element. Because $A_{sj}^2\beta_{rs}^2$ is nearly independent of the position of the substituent, δE_i is proportional to $A_{ri}^2/(E_i - E_j)$.

Applied to methoxy substitution, for which $E_j = -14.79$ eV, the values of A_{ri} given in Table 2 predict an enlargement of Φ_{dhp} on *para-* and *meta*-substitution but the measured values of Φ_{dhp} are clearly smaller than for (4a). On substitution at C-4, -5, and -4′, a lowering of Φ_{dhp} is predicted, which is indeed found. The predicted decrease of Φ_{dhp} on substitution at C-3′ (or C-5′) is again contrary to the experimental results.

For the other substituents similar contradictions emerge between theoretical and experimental results. So, it appears that the method of Muszkat and Schmidt does not give even a qualitative explanation for substituent effects on the cyclization of (4) to (6), much less for the Hammett plot we found.*

Another explanation of the measured substituent effects is based on the supposition, previously applied,[8a,14] that the internal conversion from the S_1 state of the reactant to the S_0 state of the product is the essential step for substituent effects. Therefore, potential energy curves for the S_0 and S_1 states during conrotatory cyclization from (4a) to (5a) were drawn on the basis of qualitative MO arguments (see Figure 2). It is known that such energy diagrams based on extended Hückel MO calculations[9] or MINDO methods[15] do not give better results.[16,17]

For the reaction co-ordinate we used the distance between C-2′ and the vinyl β-carbon in (4a) [or C-8a and -9 in (5a)]. This distance was varied from 2.70 Å, where the overlap between the orbitals of C-2′ and -β begins to occur,[9,10] and 1.53 Å, the distance between C-8a and -9 in (5a). At these extremes S_0 has a minimum, which is higher in (5a) than in (4a) as a consequence of the loss of resonance energy.

Starting from 2.70 Å the energy in the ground state increases because electrons are withdrawn from a binding orbital of the π-electron system. Starting from 1.53 Å the energy in the ground state increases because a σ-bond is broken. These two curves will cross at *ca.* 2 Å, where configurational interaction leads to some lowering of energy (for a polyene this lowering of energy is expected to be *ca.* 5 kcal mol^{-1}).[9]

In the excited state at 2.70 Å one π-electron from the HOMO has been promoted to the anti-bonding LUMO. Decreasing the distance results in the formation of a new bond with a net energy gain.[9,10] Starting from the excited state of (5a) at 1.53 Å an interaction with the π-electrons in the HOMO and LUMO will coincide with the breaking of the σ-bond between C-8a and -9, resulting in a decrease of energy. Therefore, in the excited state a minimum will occur at *ca.* 2 Å.[16]

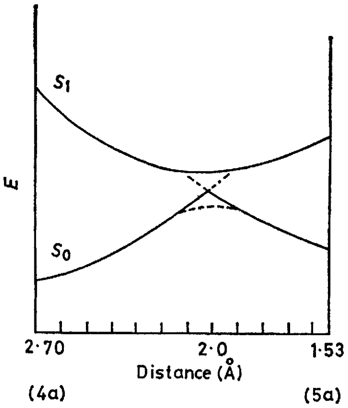

FIGURE 2 Potential energy curves for the S_0 and S_1 states during conrotatory cyclization from (4a) to (5a)

In the absorption spectra of (4a) $\lambda_{\text{max.}}$ is nearly equal for all compounds.[1] This means that the energy difference between the HOMO and LUMO of (4) is little influenced by substituents.

A substituent effect on the i.s.c. is improbable, considering the limited (or totally absent) effect on the spin–orbit coupling of the substituents used.[2] An effect on the i.s.c. is made even more improbable by the following facts. First, the effect of oxygen on Φ_{dhp} is very small, while oxygen is known to enhance the i.s.c. efficiency. Secondly, in the preceding paper[1] we demonstrated that the *trans–cis* and *cis–trans* isomerizations of (4) proceed *via* the triplet state. An effect on the i.s.c. should therefore be reflected in the $c:t$ ratios, but no relation has been found between $c:t$ ratios and Φ_{dhp}.

Therefore, a qualitative explanation of substituent effects has to be sought in variations in the curves in the

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* In the meantime Muszkat and Schmidt have also questioned the applicability of extended Hückel calculations for this purpose.[9b]

[14] P. H. G. op het Veld and W. H. Laarhoven, *J.C.S. Perkin II*, 1977, 268.

[15] (*a*) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1285; (*b*) N. C. Baird, *Chem. Comm.*, 1970, 199.

[16] J. Michl, *Topics Current Chem.*, 1974, **46**, 1.

[17] A. Devaquet, *J. Amer. Chem. Soc.*, 1972, **94**, 5160.

neighbourhood of the energy minimum of the S_1 and the maximum of the S_0 state (Figure 3) where the radiationless decay from the S_1 to the S_0 state proceeds by ' tunnelling '.[18] Competition between the relaxation to the reactant (4) [internal conversion (i.c.)] and to the product (5) determines the quantum yield of the reaction.[19]

We suppose, that substituents can change the position and height of the maximum in S_0 (see S_0' in Figure 3) as well as the minimum in S_1 (S_1' in Figure 3). This will be reflected in the rates (and quantum yields) of internal conversion and product formation. Because the quantum yields of these two processes are complementary (accepting that the $\Phi_{\text{i.s.c.}}$ is independent of the substituents) the effect on $k_{\text{cycl}}/k_{\text{i.c.}}$ is larger than on the individual reaction rates. In view of the experimentally found Hammett relation between $k_{\text{cycl}}/\Sigma k_{\text{D}}$ and σ values for the ground state we tentatively conclude that the main effect of substituents is on the position and height of the maximum in the *ground state*.

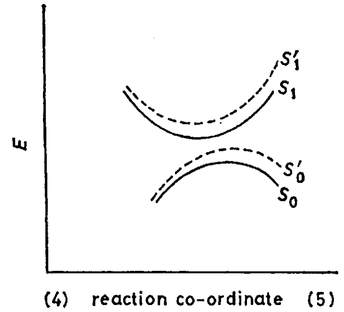


FIGURE 3 Plot of energy of S_0, S_0', S_1, and S_1', against reaction co-ordinate for conversion of (4) and (5)

It is not quite clear in which way the positive value of ρ for the Hammett relation should be interpreted. A possible explanation may be that in compounds with electron-withdrawing substituents the loss of resonance energy is smaller than in the unsubstituted compound. The maximum in S_0 and k_{cycl} will then be lower. For an electron-donating substituent the reverse should be true.

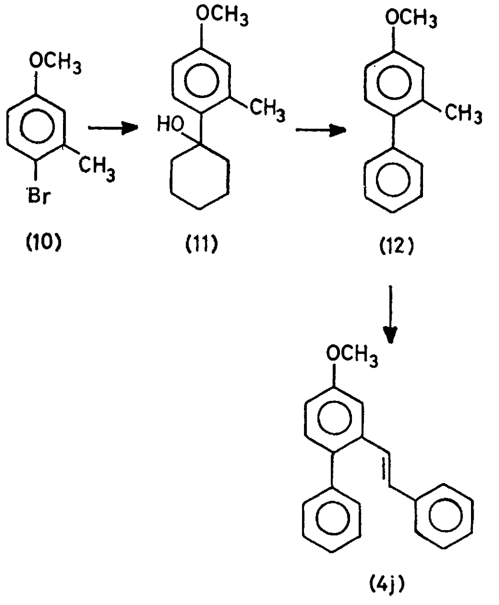
EXPERIMENTAL

For general methods see ref. 1. Quantum yields were measured using a black box similar to that described by Zimmermann.[20] Ferrioxalate actinometry, with the modification described by Murov,[12] was used to measure the light intensity. For the filter system we used a three compartment cell, each compartment with an optical path-length of 2 cm and fitted with quartz windows. The compartments were filled with respectively a 2M-$NiSO_4$ solution in 5% H_2SO_4, a 0.8M-$CoSO_4$ solution in 5% H_2SO_4, and a 0.012M-$Bi(NO_3)_3$ solution in 2 : 3 HCl–H_2O. The transmission of this filter system is $<1\%$ below 265 and above 302 nm and the maximum transmission is 16% at 286 nm.

Because the absorption bands of (4) and (6) in the u.v. spectra overlap, the n.m.r. spectra were used for the calculation of the quantum yields. To check the accuracy of this method the n.m.r. spectra of mixtures of (4) and (6) of known composition were taken and these spectra were integrated electronically. The compositions calculated from these spectra were identical with the known compositions within the accuracy of measurement. Only conversions up to 20% have been used; therefore, $\Phi_{cis\text{-}trans}$ and $\Phi_{trans\text{-}cis}$ had not to be corrected for the reverse reaction. The deviation in these values is $<10\%$. Values of Φ_{dhp} and Φ_{phe} were determined for equilibrium mixtures of *cis*- and *trans*-(4). The deviation in these values is also $<10\%$. Φ_{phe} was measured under oxygen, Φ_{ct} and Φ_{tc} under argon, and Φ_{dhp} under both conditions.

Substrates.—The syntheses and physical data of the 2-(β-arylvinyl)biphenyls (4a—i) are described in ref. 1.

4-*Methoxy*-2-*styrylbiphenyl* (4j).—The synthesis of this compound was carried out as shown in Scheme 3. 2-Bromo-5-methoxytoluene (10) was synthesized according to the literature.[21] The compound was converted into 1-(4-methoxy-2-methylphenyl)cyclohexanol (11) by a Grignard reaction with n-butyl-lithium and cyclohexanone.[22] Dehydration of (11) with formic acid [22] and subsequent oxidation with dichlorodicyanoquinone [23] yielded 4-methoxy-2-methylbiphenyl (12). With *N*-bromosuccinimide and triphenylphosphine a phosphonium salt was prepared, which in a Wittig reaction with benzaldehyde yielded 4-methoxy-2-styrylbiphenyl (4j). The Wittig reaction (yield 96%) was carried out according to Markl and Merz.[24] The *cis*- and *trans*-isomers were separated by column chromatography over Al_2O_3, using a gradient of hexane and toluene as eluant. *cis*-4-Methoxy-2-styrylbiphenyl *cis*-(4j) was an oil, $\lambda_{\text{max.}}(CH_3OH)$ 283 (log ε 4.12), 256 (4.27), and 218 nm



SCHEME 3

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[18] R. C. Dougherty, *J. Amer. Chem. Soc.*, 1971, **93**, 7187.

[19] J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, 1969, **7**, 149.

[20] H. E. Zimmermann, *Mol. Photochem.*, 1971, **3**, 281.

[21] (*a*) G. Darzens and A. Levy, *Compt. rend.*, 1931, **193**, 292; (*b*) P. Hill, W. F. Short, N. Stromberg, and A. E. Wiles, *J. Chem. Soc.*, 1937, 511.

[22] N. Campbell and H. Wang, *J. Chem. Soc.*, 1949, 2186.

[23] R. T. Arnold, C. Collins, and Wm. Zenk, *J. Amer. Chem. Soc.*, 1940, **62**, 983.

[24] G. Markl and A. Merz, *Synthesis*, 1973, 295.

(4.51); $\delta(CCl_4)$ 7.62—6.51 (13 H, m), 6.47 and 6.44 (2 H, AB, *J* 12 Hz), and 3.55 (3 H, s); *m/e* 286 (100%, M^+), 255 (68), 209 (64), 195 (49), and 165 (74); *trans*-4-methoxy-2-styrylbiphenyl *trans*-(4j) was an oil, $\lambda_{max.}(CH_3OH)$ 298 (log ε 4.33), 258 (4.33), and 220 nm (4.42); $\delta(CCl_4)$ 7.69—6.82 (13 H, m), 7.07 and 7.05 (2 H, AB, *J* 16 Hz), and 3.55 (3 H, s): mass spectrum identical with that of *cis*-(4j).

5-*Methoxy*-2-*styrylbiphenyl* (4k).—2-Bromo-4-methoxytoluene was synthesized starting *p*-nitrotoluene.[25–27] The Grignard reaction with cyclohexanone was carried out as described by Stiles and Sisti.[28] The further reactions were effected as described for (4j). The yield of the Wittig reaction was 55%. *cis*-5-Methoxy-2-styrylbiphenyl *cis*-(4k) was an oil, $\lambda_{max.}(CH_3OH)$ 296 (log ε 4.11) and 225 nm (4.47); $\delta(CCl_4)$ 7.60—6.56 (13 H, m), 6.39 and 6.36 (2 H, AB, *J* 12 Hz), and 3.79 (3 H, s); *m/e* 286 (100%, M^+), 209 (41), 195 (47), and 165 (90); *trans*-5-methoxy-2-styrylbiphenyl *trans*-(4k) was an oil, $\lambda_{max.}(CH_3OH)$ 312 (log ε 4.41), 249 (4.17), and 221 nm (4.37); $\delta(CCl_4)$ 7.71—6.58 (13 H, m), 6.99 and 6.95 (2 H, AB, *J* 16 Hz), and 3.81 (3 H, s); mass spectrum identical with that of *cis*-(4k).

3′-*Methoxy*-2-*styrylbiphenyl* (4l).—The synthesis of (4l), starting with a Grignard reaction between *m*-bromoanisole and 2-methylcyclohexanone, was analogous to that of (4k). The yield of the Wittig reaction was 68%. *cis*-3′-Methoxy-2-styrylbiphenyl *cis*-(4l) was an oil, $\lambda_{max.}(CH_2OH)$ 275 (log ε 4.14) and 246 nm (4.16); $\delta(CCl_4)$ 7.64—6.66 (14 H, m), 6.48 and 6.46 (2 H, AB, *J* 12 Hz), and 3.76 (3 H, s); *m/e* 286 (100%, M^+), 255 (56), 209 (59), 195 (87), and 165 (40); *trans*-3′-methoxy-2-styrylbiphenyl *trans*-(4l) was an oil, $\lambda_{max.}(CH_3OH)$ 301 (log ε 4.39) and 251 nm (4.18); $\delta(CCl_4)$ 7.87—6.67 (13 H, m), 7.10 and 7.07 (2 H, AB, *J* 16 Hz), and 3.77 (3 H, s); mass spectrum identical with that of *cis*-(4l).

4′-*Methoxy*-2-*styrylbiphenyl* (4m).—The synthesis of this compound was carried out as for (4l) with *p*-bromoanisole as the starting compound. The yield of the Wittig reaction was 95%. *cis*-4′-Methoxy-2-styrylbiphenyl *cis*-(4m) was an oil, $\lambda_{max.}(CH_3OH)$ 282 (log ε 4.23), 259 (4.32), and 221 nm (4.45); $\delta(CCl_4)$ 7.42—6.82 (13 H, m), 6.46 and 6.44 (2 H, AB, *J* 12 Hz), and 3.80 (3 H, s); *m/e* 286 (100%, M^+), 255 (68), 209 (64), 195 (49), and 165 (74); *trans*-4′-methoxy-2-styrylbiphenyl *trans*-(4m) was an oil, $\lambda_{max.}(CH_3OH)$ 300 (log ε 4.39), 263 (4.35), and 223 nm (4.33); $\delta(CCl_4)$ 7.78—6.60 (13 H, m), 7.10 and 7.07 (2 H, AB, *J* 16 Hz), and 3.84 (3 H, s); mass spectrum identical with that of *cis*-(4m).

Irradiation Products.—The general procedure for preparative irradiations has been described elsewhere.[1] The physical constants of the 9,10-dihydrophenanthrenes from (4a—l) are also given in ref. 1.

2-Methoxy-9-phenyl-9,10-dihydrophenanthrene has m.p. 78—80°; $\lambda_{max.}(CH_3OH)$ 280 nm (log ε 4.29); $\delta(CCl_4)$ 7.96—6.60 (12 H, m), 4.16 (1 H, X part of ABX, *J* 8 Hz), 3.20 and 3.12 (2 H, d, AB of ABX), and 3.79 (3 H, s); *m/e* 286 (100%, M^+), 255 (21), 209 (27), 194 (48), and 165 (77). 3-Methoxy-9-phenyl-9,10-dihydrophenanthrene was an oil, $\lambda_{max.}(CH_3OH)$ 307 (log ε 3.76), 270 (4.08), and 262 nm (4.15); $\delta(CCl_4)$ 8.00—6.62 (12 H, m), 4.16 (1 H, X part of ABX, *J* 8 Hz), 3.17 and 3.09 (2 H, d, AB of ABX), and 3.85 (3 H, s); *m/e* 286 (100%, M^+), 255 (28, 209 (56), 194 (36), and 165 (78). Irradiation of (4l) yielded the two products in the ratio 2 : 1. 6-Methoxy-9-phenyl-9,10-dihydrophenanthrene, the major product, was an oil, $\lambda_{max.}(CH_3OH)$ 305 (log ε 3.79) and 261 nm (4.20); $\delta(CCl_4)$ 7.96—6.58 (12 H, m), 4.12 (1 H, X part of ABX, *J* 8 Hz), 3.19 and 3111 (2 H, d, AB of ABX), and 3.82 (3 H, s); *m/e* 286 (16%, M^+), 255 (10), 209 (75), and 165 (100). 8-Methoxy-9-phenyl-9,10-dihydrophenanthrene, the minor product, was an oil, $\lambda_{max.}(CH_3OH)$ 285 (log ε 3.95) and 2.70 nm (4.16); $\delta(CCl_4)$ 7.96—6.71 (12 H, m), 4.78—4.63 (1 H, m, X part of ABX), 3.50 and 2.93 (2 H, m, AB of ABX), and 3.76 (3 H, s); *m/e* 286 (11%, M^+), 255 (7), 209 (43), 194 (50), and 165 (100). 7-Methoxy-9-phenyl-9,10-dihydrophenanthrene had m.p. 71—73 °C; $\lambda_{max.}(CH_3OH)$ 279 nm (log ε 4.26); $\delta(CCl_4)$ 7.89—6.38 (12 H, m), 4.13 (1 H, X part of ABX, *J* 8 Hz), 3.19 and 3.11 (2 H, d, AB of ABX), and 3.96 (3 H, s); *m/e* 286 (97%, M^+), 255 (24), 209 (36), 194 (32), and 165 (100).

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