Synthetic and Mechanistic Aspects of the Photocyclization of 2-(β-Arylvinyl)biphenyls into 9-Aryl-9,10-dihydrophenanthrenes

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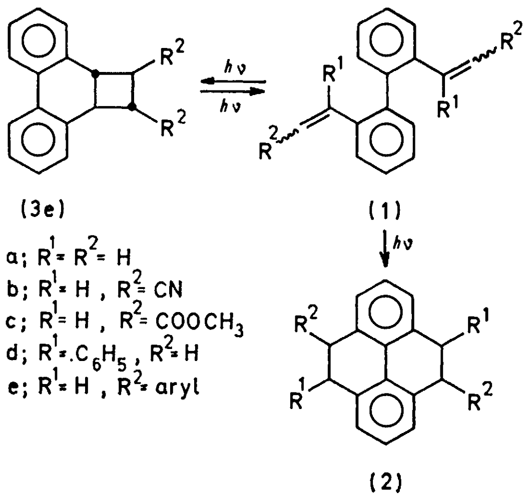
The synthesis is described of several 2-(β-arylvinyl)biphenyls (4c), some of which contain deuterium on C-2'—6' (14c). On irradiation they yield 9-aryl-9,10-dihydrophenanthrenes (6c) in which the isotope if present is found on C-5—8 and at the *cis*- or *trans*-position of C-10 (15c). The photoreaction consists of a stereoselective, probably concerted, conrotatory cyclization from the S_1 state of both *cis*- and *trans*-(4c) to a 9-aryl-8a,9-dihydrophenanthrene derivative (5c), followed by a thermal, suprafacial [1,5] sigmatropic hydrogen shift. The rate of the hydrogen shift is so fast that (5c) cannot be detected spectroscopically in the reaction mixture and equally is not oxidized by dissolved oxygen to a 9-arylphenanthrene (9c), which does arise in the presence of iodine as oxidant.

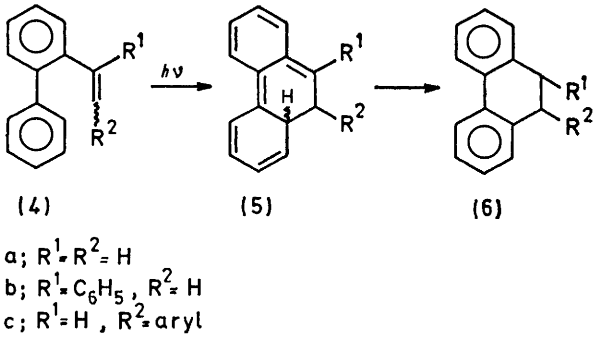
THE photocyclization of 2,2'-divinylbiphenyl (1a) into 4,5,9,10-tetrahydropyrene (2a) has been described by Padwa and Mazzu[1] and by op het Veld *et al.*[2] Irradiation of the related compounds (1b—d) gives similar products (2b—d). For (1e), however, the photochemical behaviour changes. In this case irradiation yields primarily the cyclobutane (3e) as the kinetic product, which on irradiation with light of suitable wavelength is in equilibrium with (1e). Only prolonged irradiation finally yields 4,9-diaryl-4,5,9,10-tetrahydropyrene (2e), whose formation is irreversible.[2-4]



SCHEME 1

Padwa and Mazzu have shown that the reaction (1a) ⟶ (2a) proceeds *via* two successive photocyclizations, which probably take place from the first excited singlet state (S_1) of (1a) and the intermediate 4-vinyl-9,10-dihydrophenanthrene, respectively. In a previous paper[4] we demonstrated that the intramolecular photoaddition (1e) ⟶ (3e) proceeds as a concerted $[\pi2_s + \pi2_s]$ reaction from the S_1 state of *trans,trans*-(1e), and we gave experimental evidence that the reaction (1e) ⟶ (2e) also proceeds *via* the S_1 state of (1e).

The comparable photocyclizations of 2-vinylbiphenyl (4a) into 9,10-dihydrophenanthrene (6a) and of 4-vinylphenanthrene (7) into 4,5-dihydropyrene (8) have been described by Horgan *et al.*[5] They found that these reactions take place even in the presence of oxygen.



SCHEME 2

In the former case 8a,9-dihydrophenanthrene (5a) was supposed to be an intermediate. Apparently it is not affected by oxygen in contrast to the isomeric 4a,4b-dihydrophenanthrene which gives phenanthrene under these circumstances.[6]

Irradiation of 2-(α-phenylvinyl)biphenyl (4b) gave a similar product, 9-phenyl-9,10-dihydrophenanthrene (6b).[7] Irradiation of (4b) with triplet sensitizers suggests that its cyclization proceeds *via* the triplet state. Oxygen quenches the reaction and does not lead to oxidation to 9-phenylphenanthrene. This oxidation did occur on irradiation of 2-styrylbiphenyl (4ci) in the presence of I_2 as an oxidant; nearly equal amounts of 9-phenylphenanthrene (9ci) and 1-phenylphenanthrene (10ci) were isolated.[8]

We have extended these data from the literature by a study of the photochemistry of a series of 2-(β-arylvinyl)-biphenyls (4c). In this paper the syntheses are described and mechanistic aspects of their photocyclizations discussed. The influence of substituents on the photochemical behaviour of (4c) is analysed in the following paper.

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[1] A. Padwa and A. Mazzu, *Tetrahedron Letters*, 1974, **4471**.

[2] P. H. G. op het Veld, J. C. Langendam, and W. H. Laarhoven, *Tetrahedron Letters*, 1975, 231.

[3] W. H. Laarhoven and Th. J. H. M. Cuppen, *J.C.S. Perkin I*, 1972, 2074.

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

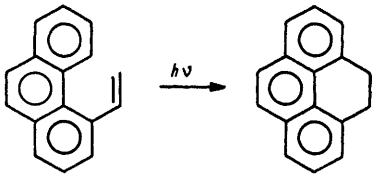
[5] S. W. Horgan, D. D. Morgan, and M. Orchin, *J. Org. Chem.*, 1973, **38**, 3801.

[6] (*a*) K. A. Muszkat and E. Fischer, *J. Chem. Soc.* (*B*), 1967, 662; (*b*) Ch. Goedicke and H. Stegemeyer, *Chem. Phys. Letters*, 1972, **17**, 492.

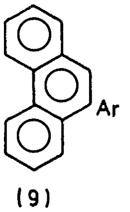
[7] R. Lapouyade, R. Koussini, and J. C. Rayez, *J.C.S. Chem. Comm.*, 1975, 676.

[8] R. J. Hayward and C. C. Leznoff, *Tetrahedron*, 1971, **27**, 5115.

Substrates.—The synthesis of the 2-(β-arylvinyl)-biphenyls (4c) started from biphenyl-2-carboxylic acid, which on reduction with $LiAlH_4$ yielded 2-hydroxymethylbiphenyl.[9] This compound was converted with HBr into 2-bromomethylbiphenyl,[10] which reacted with triphenylphosphine in xylene to give the triphenylphosphonium salt (12).[11] Compounds (4c) were obtained by a Wittig reaction [12] between this salt (12) and the appropriate aromatic aldehydes (13) (Scheme 3). For the investigation of the mechanism of the photocyclization (4c) ⟶ (6c) some deuteriated derivatives (14c) of (4c) were synthesized as shown in Scheme 4. The relevant data for these syntheses are given in Table 1 and in the Experimental section. The deuterium content and purity of the products (14c) were checked by n.m.r. and mass spectrometry and by comparison with the corresponding compounds (4c) (Table 2).



(7) (8)



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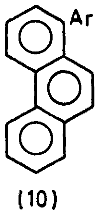

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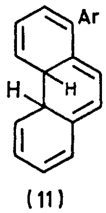

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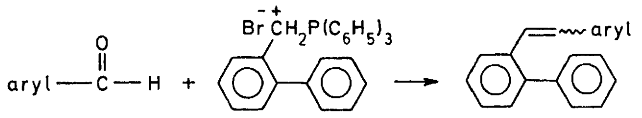

(13) (12) (4c)

aryl: i; phenyl
ii; β-naphthyl
iii; *p*-methoxyphenyl
iv; *p*-methylphenyl
v; *p*-chlorophenyl
vi; *p*-nitrophenyl
vii; *m*-methoxyphenyl
viii; *m*-methylphenyl
ix; *m*-chlorophenyl

SCHEME 3

Irradiations.—*A priori* there are, apart from the *cis–trans* isomerization, two photoreactions possible with (4c) (see Scheme 5): (i) cyclization of the stilbene ⟶ phenanthrene type, (4c) $\xrightarrow{h\nu}$ (11c) $\xrightarrow{\text{ox}}$ (10c); and (ii) intramolecular cycloaddition, analogous to (4a) ⟶ (6a), *viz.* (4c) $\xrightarrow{h\nu}$ (5c) ⟶ (6c); in this case the oxidation (5c) ⟶ (9c) might be a side-reaction.

Irradiation of (4c) at 300 nm under non-oxidative conditions in different solvents (hexane, benzene, or alcohols) and at concentrations of 10^{-2}—10^{-5}M gave always the corresponding 9-aryl-9,10-dihydrophenanthrenes (6c). These were purified by column chromatography on Al_2O_3 and recrystallized from methanol. Yields of pure (6c) were between 80 and 90%. The products were identified by spectral data and by comparison of physical constants with data from the literature (Table 3). In some cases (6ci and iii) additional proof of structure was obtained by conversion into the known 9-arylphenanthrenes (9ci and iii).

The n.m.r. spectra of the products (6c) show, besides the absorptions of aromatic protons and substituents, a distinctive pattern for the absorptions of the protons at C-9 and -10. For several compounds this pattern consists of a triplet from 9-H at δ *ca.* 4 (J 7.5 Hz), and a doublet from 10-H_2 at δ *ca.* 3 (J 7.5 Hz). This is an example of a 'deceptively simple spectrum' [13] derived from an ABX system. According to the general analysis of Bernstein *et al.*[14] in such a case only the value of $J_{AX} + J_{BX}$ can be derived from the n.m.r. spectrum. For compounds (6c) this value, measured in CCl_4, is thus 15 Hz.

For the products (6ci, ii, and viii) the AB part of the n.m.r. spectrum consists of more lines, enough to make it possible to determine the individual values of the different coupling constants and the chemical shifts, by using a computer simulation program.[15] These values are given in Table 4.

The deuteriated compounds (14ci—iii) were irradiated under identical conditions and the products (16ci—iii) purified as described for the non-deuteriated compounds. The n.m.r. and mass spectra showed that deuterium is 100% incorporated into C-10 (Table 5). It could be deduced from the n.m.r. data that two isomeric photoproducts originate from the irradiation of (14c): *cis*-(16c), having 9-aryl and 10-D *cis*, and *trans*-(16c), with these groups *trans*.

The assignment of the absorptions of the 9- and 10-H to the individual isomers was made on the basis of temperature dependent n.m.r. spectra, measured in CS_2 from +30 to −50 °C. It appeared that one coupling remains constant at 5.3 Hz for all three compounds, while the other increases by *ca.* 1 Hz in going from +30 to −50 °C.

In solution two limiting conformations exist for both the *cis*- and *trans*-isomer, one with the aryl group in a pseudoaxial (pa) and the other with the aryl group in a pseudoequatorial (pe) position (Scheme 7). In both conformers of *cis*-(16c) H_A and H_X have a pe–pa interaction. This makes J_{AX} independent of the position of the conformational equilibrium. In *trans*-(16c), however, the interaction between H_B and H_X is pe–pe in the pa conformer, but pa–pa in the pe conformer. Lowering of the temperature will induce a shift in the conform-

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[9] St. Goldschmidt and W. L. C. Veer, *Rec. Trav. chim.*, 1948, **67**, 489.

[10] J. von Braun and G. Manz, *Annalen*, 1929, **468**, 275.

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

[12] 'Organic Reactions 14,' ed. C. Cope, Wiley, New York, 1965, p. 270.

[13] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.

[14] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Canad. J. Chem.*, 1957, **35**, 65.

[15] Calculated on BNC-28 with program ITRCAL (Bruker).

ational equilibrium that will be reflected in J_{BX}. This makes it possible to assign the absorptions of H_A and H_B and to determine the *cis*:*trans* ratio by peak integration.

TABLE 1

A Methods of synthesis, yields, elemental analyses, and mass spectral data of compounds (4c)

Compound[a]	Method of synthesis[a]	Yield (%)	Required C (%)	Required H (%)	Found C (%)	Found H(%)	*m/e* (%)
(4ci)	A_1	50	93.7	6.3	94.05	6.4	256 (M^+, 67), 179 (70), 178 (100), 165 (89); *T* 70 °C
	A_2	85					
(4cii)	B	80	94.1	5.9	94.3	6.1	306 (M^+, 100), 179 (18), 178 (50); *T* 110 °C
(4ciii)	A_1	90	88.1	6.35	88.15	6.4	286 (M^+, 100), 255 (19), 179 (25), 178 (64); *T* 140 °C
(4civ)	B	82	93.3	6.7	93.0	6.7	270 (M^+, 100), 255 (24), 179 (14), 178 (29); *T* 180 °C
(4cv)	A_1	63	82.6	5.2	82.95	5.25	292/290 (M^+, 100), 255 (14), 179 (16), 178 (16); *T* 100 °C
(4cvi)	B	70	79.7 (N, 4.65)	5.0	80.05 (N, 4.7)	5.05	301 (M^+, 100), 255 (10), 179 (17), 178 (10); *T* 110 °C
(4cvii)	A_1	40	88.1	6.35	87.85	6.15	286 (M^+, 100), 255 (7), 179 (18), 178 (34); *T* 130 °C
	B	80					
(4cviii)	A_1	76	93.3	6.7	92.75	6.7	270 (M^+, 100), 255 (17), 179 (16), 178 (30); *T* 85 °C
(4cix)	A_1	53	82.6	5.2	82.25	5.25	292/290 (M^+, 100), 155 (16), 179 (23), 178 (20); *T* 135 °C

B M.p.s and n.m.r. and u.v. spectra of compounds (4c)

Compound[a]		M.p. (°C)	Chemical shift δ[b]				$\lambda_{max.}$/nm (log ε)[c]
			3-H	Aromatic H	Olefinic H	Other	
(4ci)	*cis*	Oil		7.45—6.93 (14 H, m)	6.42, 6.36 (2 H, AB, *J* 12 Hz)		284 (4.11), 249 (4.22), 219 (4.46)
	trans	Oil	7.78—7.56 (1 H, m)	7.56—7.04 (13 H, m)	7.03, 6.93 (2 H, AB, *J* 16 Hz)		[329 (3.95)], [312 (4.32)], 298 (4.37), 251 (4.22), 219 (4.38)
(4cii)	*cis*	126.5—129		7.70—7.15 (16 H, m)	6.56, 6.40 (2 H, AB, *J* 12 Hz)		301 (4.43), [275 (4.51)], 268 (4.54), 245 (460)
	trans	122—123		7.80—7.16	7.09 (2 H, s)		[340 (4.24)], 315 (4.57), 282 (4.61), 272 (4.62), 252 (4.54)
(4ciii)	*cis*	Oil		7.49—6.56 (13 H, m)	6.35, 6.24 (2 H, AB, *J* 12 Hz)	3.68 (3 H, s)	289 (4.19), 257 (4.14), [223 (4.47)]
	trans	64—67	7.71—7.53 (1 H, m)	7.40—6.66 (12 H, m)	6.88 (2 H, s)	3.67 (3 H, s)	[335 (4.18)], [321 (4.44)], 295 (4.51), 264 (4.42)
(4civ)	*cis*	63—66		7.50—6.74 (13 H, m)	6.34, 6.27 (2 H, AB, *J* 12 Hz)	2.20 (3 H, s)	285 (4.15), 251 (4.10), 220 (4.47)
	trans	46.5—48.5	7.74—7.54 (1 H, m)	7.50—6.90 (12 H, m)	6.97, 6.89 (2 H, AB, *J* 16 Hz)		[333 (4.11)], [317 (4.41)], 303 (4.45), 253 (4.27), 224 (4.39)
(4cv)	*cis*	71—72		7.40—7.02 (13 H, m)	6.38 (2 H, s)		286 (4.18), 250 (4.20), 222 (4.47)
	trans	55—58	7.65—7.50 (1 H, m)	7.33—7.03 (12 H, m)	6.97, 6.83 (2 H, AB, *J* 16 Hz)		[335 (4.01)], [317 (4.38)], 301 (4.44), 254 (4.27), 224 (4.32)
(4cvi)	*cis*	122.5—123		7.94—7.05 (13 H, m)	6.60, 6.47 (2 H, AB, *J* 12 Hz)		323br (4.07), 235 (4.29)
	trans	101—102	7.72—7.50 (1 H, m)	8.01—7.15 (12 H, m)	7.17, 6.97 (2 H, AB, *J* 16 Hz)		338br (4.09), 237 (4.32)
(4cvii)	*cis*	Oil		7.38—6.49 (13 H, m)	6.35 (2 H, s)	3.47 (3 H, s)	287 (3.94), 248 (4.07), [226 (4.27)]
	trans	Oil	7.65—7.47 (1 H, m)	7.37—6.50 (12 H, m)	6.99, 6.86 (2 H, AB, *J* 16 Hz)	3.61 (3 H, s)	[335 (3.64)], [320 (4.03)], 299 (4.22), 245 (4.23), 225 (4.41)
(4cviii)	*cis*	51—52		7.52—6.78 (12 H, m)	6.38, 6.34 (2 H, AB, *J* 12 Hz)	2.22 (3 H, s)	284 (4.18), 248 (4.29), [221 (4.55)]
	trans	Oil	7.65—7.51 (1 H, m)	7.40—6.79 (12 H, m)	6.97, 6.85 (2 H, AB, *J* 16 Hz)	2.25 (3 H, s)	[331 (3.90)], [316 (4.28)], 301 (4.34), 250 (4.23), 220 (4.40)
(4cix)	*cis*	Oil		7.36—6.88 (13 H, m)	6.42, 6.30 (2 H, AB, *J* 12 Hz)		282 (4.13), 252 (4.16), 221 (4.46)
	trans	Oil	7.69—7.52 (1 H, m)	7.43—7.08 (12 H, m)	7.04, 6.86 (2 H, AB, *J* 16 Hz)		[331 (3.94)], [316 (4.27)], 300 (4.36), 249 (4.21), 220 (4.36)

[a] See Experimental section. [b] Measured in CCl_4, with Me_4Si as internal reference. [c] Measured in methanol.

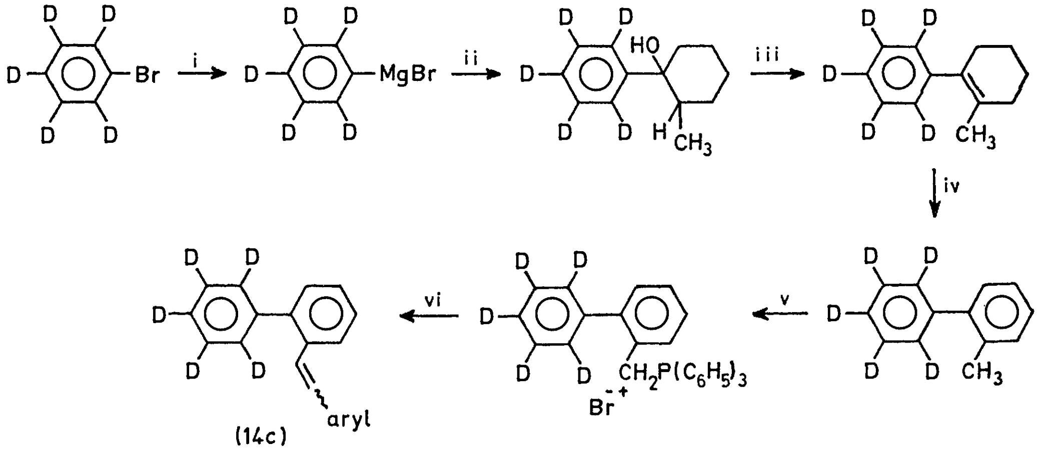
TABLE 2

M.p.s and mass and n.m.r. spectral data of compounds (14c)

Compound	M.p. (°C)	*m/e* (parent ion)	Chemical shift δ[a]		
			3-H	Aromatic H	Olefinic H
trans-(14ci)	Oil	261	7.8—7.6 (1 H, m)	7.5—7.1 (8 H, m)	7.0 and 6.9 (2 H, AB, *J* 16 Hz)
trans-(14cii)	121—122	311		7.8—7.15 (11 H, m)	7.1 (2 H, s)
trans-(14ciii)	65—67	291	7.7—7.5 (1 H, m)	7.4—6.6 (7 H, m)	6.9 (2 H, s)

[a] Measured in CCl_4, with Me_4Si as internal reference.

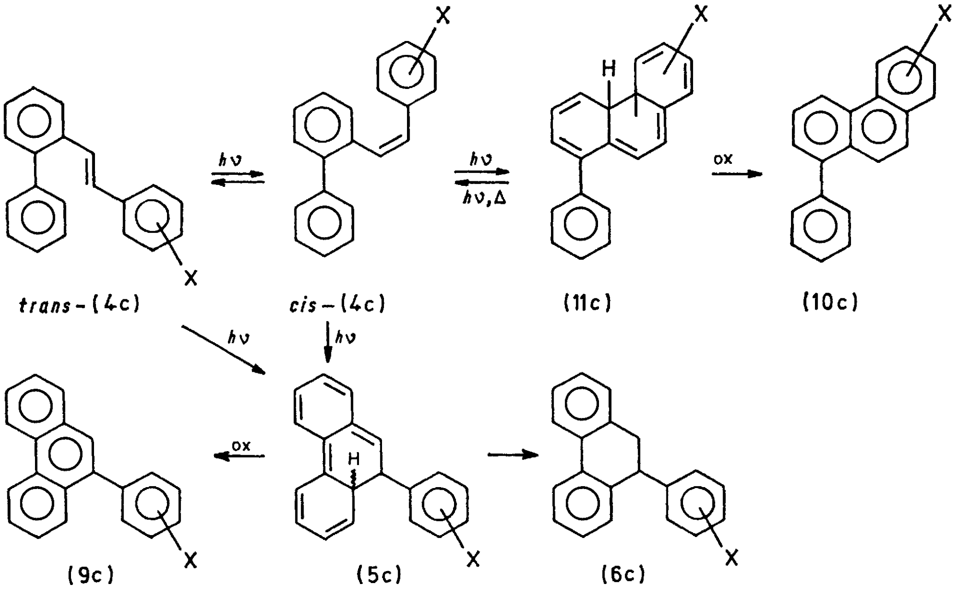
If the values of J_{pa-pa} and J_{pe-pe} are known the population of the two conformations can be calculated [16] according to equation (1), where x is the fraction of the conformation with the aryl group pseudoequatorial.



SCHEME 4 Reagents: i, Mg; ii, 2-methylcyclohexanone; iii, $-H_2O$; iv, DDQ; v, *N*-bromosuccinimide, then $P(C_6H_5)_3$; vi, aryl CHO

$$J_{BX} = xJ_{pa-pa} + (1 - x)J_{pe-pe} \qquad (1)$$

From ^{13}C satellite resonances of 9,10-dihydrophenanthrene (6a), measured by Cohen *et al.*,[17] values of 5.8 Hz for J_{pa-pe} and 16.6 Hz for $J_{pa-pa} + J_{pe-pe}$ were calculated. The former value corresponds very well with those found for J_{AX} for (6c) (*ca.* 5.4 Hz, Table 4) and for (16c) (5.3 Hz, Table 5).



SCHEME 5

For J_{pe-pe} a value of 2.0 Hz was proposed,[16] which makes J_{pa-pa} 14.6 Hz. From these values x was calculated for several products (6c) and (16c) (Tables 4 and 5). There appears to be, at room temperature, a small preference by the aryl group for the pseudoequatorial position. This is in marked contrast to the results of Harvey *et al.*[16] They ascribe the preference of several substituents (*e.g.* t-butyl or trimethylsilyl) at C-9 of (6) for the pseudoaxial position to a *peri*-interaction between the substituent and H-8.* The difference may be caused by the much larger and ' harder ' substituents used by Harvey by comparison with the aryl groups in our study.

When (4c) was irradiated in the presence of oxygen a nearly equal amount of a 1-phenylphenanthrene (10c) was formed in addition to (6c). Compounds (4c)

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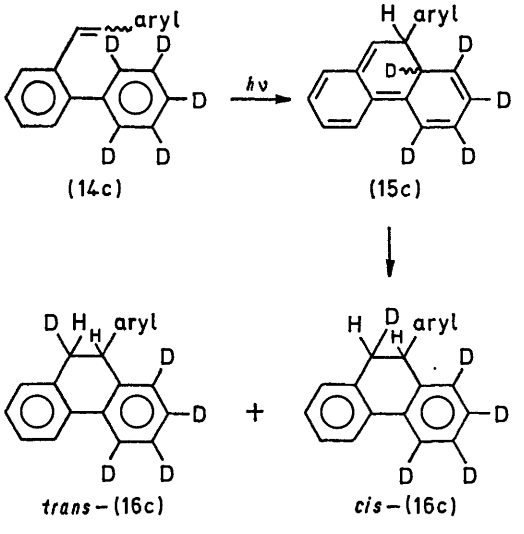
* On the basis of our measurements and those of Cohen *et al.*[17] a value close to 5.8 Hz for J_{pa-pe} seems more appropriate than the 6.8 Hz used by Harvey *et al.*[16] and based on their work with dihydronaphthalenes. This does not change, however, their general conclusions.

[16] R. G. Harvey, P. P. Fu, and P. W. Rabideau, *J. Org. Chem.*, 1976, **41**, 3722.

[17] D. Cohen, I. T. Miller, H. Heany, P. R. Constantine, A. R. Katritzky, B. M. Semple, and M. J. Sewell, *J. Chem. Soc. (B)*, 1967, 1248.

having *meta*-substituents give two isomers. No trace of a 9-arylphenanthrene (9c) was found. In the presence of iodine, however, along with (10c) substantial amounts of (9c) were formed. In some cases (4cii and vii) (6c) was also obtained in 25 and 5% yield, respectively, but with the other compounds (4c) the amount of (6c) was always <1%. The reaction mixtures were analysed by n.m.r. No efforts were made at separation.



SCHEME 6

TABLE 3

M.p.s and n.m.r., u.v., and mass spectral data for compounds (6c)

Compound	M.p. (°C)		Chemical shift δ [a]					$\lambda_{max.}$/nm (log ε) [b]	*m/e* (%)
	Measured	Lit. value	Aromatic			H_A and H_B	Other		
			3-H	H	H_X				
(6ci)	80—81	79—80 [c] 82—83 [d]	7.80— 7.60 (2 H, m)	7.32— 6.60 (11H, m)	4.22— 4.01 (1 H, t)	3.20— 3.06 (2 H, m)		298 (3.57), 266 (4.21)	256 (M^+, 100), 179 (46), 178 ($M^+ - C_6H_6$, 63); *T* 50 °C
(6cii)	166—168			7.75— 6.72 (15 H, m)	4.30— 4.12 (1 H, t)	3.62— 3.02 (2 H, m)		[300 (3.65)], [273 (4.31)], 268 (4.33), 227 (5.01)	306 (M^+, 100), 179 (18), 178 ($M^+ - C_{10}H_8$, 55); *T* 160 °C
(6ciii)	107—109	106—107 [c]	7.80— 7.59 (2 H, m)	7.30— 6.60 (10 H, m)	4.15— 3.93 (1 H, t)	3.20— 3.01 (2 H, d)	3.66 (3 H, s)	298 (3.61), 267 (4.25)	286 (M^+, 100), 255 (10), 179 (20), 178 ($M^+ - C_6H_5OCH_3$, 60); *T* 100 °C
(6civ)	81.5—83.5	78—79.5 [e]	7.74— 7.53 (2 H, m)	7.30— 6.72 (10 H, m)	4.08— 3.87 (1 H, t)	3.11— 2.95 (2 H, d)	2.21 (3 H, s)	298 (3.60), 265 (4.22)	270 (M^+, 100), 255 (24), 179 (25), 178 ($M^+ - C_6H_5CH_3$, 53); *T* 90 °C
(6cv)	105—107	108—109.5	7.78— 7.57 (2 H, m)	7.33— 6.77 (10 H, m)	4.20— 3.96 (1 H, t)	3.42— 2.80 (2 H, m)		298 (3.56), 267 (4.20)	290/292 (M^+, 62), 255 (17), 253 (20), 179 (61), 178 ($M^+ - C_6H_5Cl$, 100); *T* 50 °C
(6cvi) [f]									
(6cvii)	71—73		7.72— 7.51 (2 H, m)	7.51— 6.49 (10 H, m)	4.19— 3.91 (1 H, t)	3.23— 2.99 (2 H, d)	3.57 (3 H, s)	298 (3.59), 266 (4.19)	286 (M^+, 35), 255 (9), 179 (41), 178 ($M^+ - C_6H_5OCH_3$, 100)
(6cviii)	61—62		7.79— 7.55 (2 H, m)	7.39— 6.71 (10 H, m)	4.17— 3.92 (1 H, t)	3.24— 3.01	2.25 (3 H, s)	298 (3.67), 265 (4.18)	270 (M^+, 100), 255 (11), 179 (17), 178 ($M^+ - C_6H_5CH_3$, 29); *T* 160 °C
(6cix)	56—59		7.77— 7.55 (2 H, m)	7.39— 6.71 (10 H, m)	4.23— 3.87 (1 H, t)	3.29— 2.91 (2 H, d)		298 (3.60), 266 (4.23)	290/292 (M^+, 93), 255 (19), 253 (21), 179 (90), 178 ($M^+ - C_6H_5Cl$, 100); *T* 120 °C

[a] Measured in CCl_4, with Me_4Si as internal reference. [b] Measured in methanol. [c] W. L. Dilling, *Tetrahedron Letters*, 1966, 939. [d] R. G. Harvey, P. P. Fu, and P. W. Rabideau, *J. Org. Chem.*, 1976, **41**, 3722. [e] R. N. Goerner, P. N. Cote, and B. M. Vittimberga, *J. Org. Chem.*, 1977, **42**, 19. [f] Not obtained pure enough to measure the spectral data. Only n.m.r. values are given, δ 7.5—6.9 (12 H, m), 4.0—3.7 (1 H, t), and 3.0—2.8 (2 H, m).

Mechanisms of Photoreactions.—(a) *The* cis–trans *isomerization*. Although there is no complete agreement about the mechanism of the *cis–trans* isomerization of stilbenes, reaction from the triplet state has been accepted for some derivatives.[18] The triplet energy of *trans*-stilbene is *ca.* 50 kcal and of *cis*-stilbene *ca.* 55 kcal mol^{-1}.[19] Therefore, we assume that the triplet energy of (4c) is also *ca.* 50—55 kcal mol^{-1}.

TABLE 4

Data from simulated n.m.r. spectra of compounds (6c)

Compound	Chemical shift δ [a]			Coupling constant (Hz) [a]			*x* [b]
	H_A	H_B	H_X	J_{AB}	J_{AX}	J_{BX}	
(6ci)	3.10	3.14	4.10	−15.03	5.37	9.70	0.61
(6cii)	3.115	3.20	4.20	−14.84	5.39	9.42	0.59
(6cviii)	3.06	3.15	4.04	−15.64	5.02	10.42	0.67

[a] Computed on BNC-28, with ITRCAL program (Bruker). [b] Fraction with aryl group in equatorial position (see text).

On irradiation of *trans*-(4cii and iii) and *trans*-(14cii) in the presence of azulene (E_T 31 kcal mol^{-1}) [19] *trans–cis* isomerization was suppressed. This supports the presumption that the isomerization of (4c) [and (14c)] proceeds *via* the triplet state.

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[18] (*a*) J. Saltiel, J. D'Agostinho, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, 1973, **3**, 1; (*b*) Th. Kindt, E.-P. Resewitz, Ch. Goedicke, and E. Lippert, *Z. Phys. Chem. (Frankfurt)*, 1976, **101**, 1.

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

(b) *The formation of* 9-*aryl*-9,10-*dihydrophenanthrenes* (6c). The first step in the formation of (6c) from (4c) is supposed to be the photocyclization of (4c) into 9-aryl-8a,9-dihydrophenanthrene (5c). This compound might be converted into (6c) *via* an allowed [20] thermal [1,5] sigmatropic hydrogen shift or *via* a radical chain reaction.

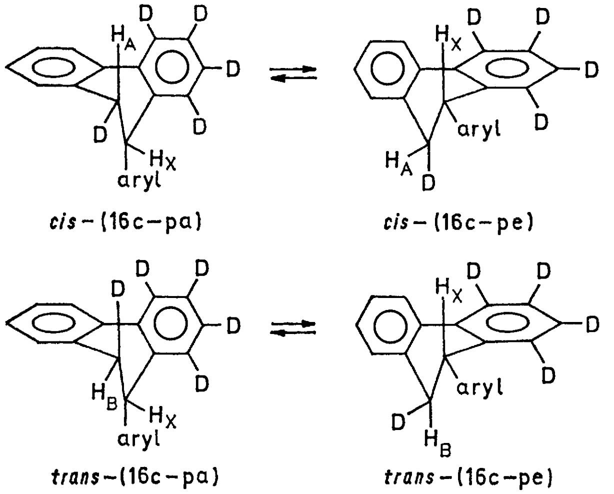
In order to establish the multiplicity of the photocyclization, compounds (4cii and iii) and (14cii) were irradiated in the presence of the triplet quencher azulene. Product formation was not suppressed. Furthermore, use of the triplet sensitizers benzil (E_T 54 kcal mol^{-1}) and benzophenone (E_T 69 kcal mol^{-1}) did not accelerate the photocyclization of (4ciii or iv). The formation of some (6ciii and iv) in these experiments can be ascribed to the competition in absorption between (4c) and the sensitizers.

TABLE 5

M.p.s and mass and n.m.r. spectral data for compounds (16c)

Compound	M.p. (°C)	*m*/*e* (%)	Isomer distribution (%) [a]	Chemical shift δ [a] H_A	H_B	H_X	Coupling constant [a] J_{AX}	J_{BX}	*x* [b]
(16ci)	80—81	261 (M^+, 100), 283 ($M^+ - C_6H_5$, 50), 282 ($M^+ - C_6H_5D$, 19); *T* 60 °C	*cis* 50	3.10		4.11	5.3		
			trans 50		3.15	4.11		10.0	0.64
(16cii)	166—168	311 (M^+, 100), 183 ($M^+ - C_{10}H_8$, 54), 182 ($M^+ - C_{10}H_7D$, 27); *T* 130 °C	*cis* 61	3.12		4.20	5.3		
			trans 39		3.19	4.20		9.5	0.60
(16ciii)	107—109	291 (M^+, 100), 183 ($M^+ - C_6H_5OCH_3$, 70), 182 ($M^+ - C_6H_4DOCH_3$, 31); *T* 110 °C	*cis* 71	3.06		4.04	5.3		
			trans 29		3.10	4.04		10.0	0.64

[a] Computed from the n.m.r. spectra in CCl_4, with Me_4Si as internal reference. [b] Fraction with aryl group in equatorial position (see text).



cis-(16c-pa) *cis*-(16c-pe)

trans-(16c-pa) *trans*-(16c-pe)

SCHEME 7

It is known that a nitro group enhances intersystem crossing $S_1 \longrightarrow T_1$.[21] The low quantum yield for the cyclization of (4cvi) (Φ 0.001) compared with the unsubstituted compound (4ci) (Φ 0.023) can therefore be seen as another indication that the reactive state for cyclization is the S_1 state.

From the complete deuterium incorporation at C-10 in (16c) on irradiation of (14c) it must be concluded that the reaction (15c) ⟶ (16c) [or (5c) ⟶ (6c)] proceeds *via* a [1,5] sigmatropic shift, and not *via* a radical reaction. According to Woodward and Hoffmann [20] this shift in a six-carbon ring compound must be a suprafacial–suprafacial process, [$\sigma 2_s + \pi 4_s$], which is symmetrically allowed under thermal conditions.

The ultimate position of the deuterium at C-10 in (16c), *cis* or *trans* with respect to the 9-aryl group, is consequently the same as in the intermediate (15c). Because both the *cis*- and *trans*-isomers of (16c) are formed the photocyclization (14c) ⟶ (15c) must also give both *cis*- and *trans*-isomers. For the formation of these two geometric isomers two explanations are possible. (i) The photocyclization (14c) ⟶ (15c) is a stereospecific, possibly a concerted process. According to the Woodward–Hoffmann rules [20] this cyclization should then be conrotatory, and (15c) should arise from the S_1 state of both *cis*- and *trans*-(14c). (ii) The photocyclization (14c) ⟶ (15c) is not stereospecific, but proceeds *via* a radical reaction. *cis*- and *trans*-(14c) each in itself may then yield a *cis*–*trans* mixture of (15c).

In order to distinguish between these two possibilities we irradiated *trans*-(14cii) in the presence of the triplet quencher azulene to suppress *trans*–*cis* isomerization. In this case only one isomer was formed, *cis*-(16cii), the isomer which should arise *via* conrotatory cyclization followed by a suprafacial [1,5] sigmatropic shift. This proves that the cyclization proceeds stereospecifically and probably in a concerted way.

The varying *cis* : *trans* ratios in products (16c) containing different substituents (Table 5) can be ascribed to different ratios in the substrates (14c). The attainment of the *cis*–*trans* equilibrium in (14c) is faster than cyclization to (16c).

As a matter of course the conclusion derived from the experiments with deuteriated compounds holds equally well for the cyclization of the non-deuteriated compounds (4c) ⟶ (6c).

It is remarkable that (5c) is not oxidized to (9c) by oxygen. This oxidation can be compared with the thermal oxidation of 4a,4b-dihydrophenanthrene by

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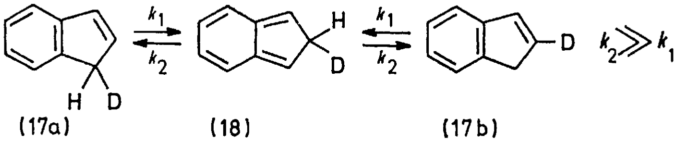
[20] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[21] M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.

oxygen. Muszkat and Fischer calculated for the latter reaction a rate of *ca.* 2 × 10^{-6} l mol^{-1} h^{-1}.[6a] The oxidation of (5c) is in principle possible, as is evident from the formation of (9c) on irradiation of (4c) in the presence of I_2. Apparently the rate of the [1,5] hydrogen shift is faster than oxidation by oxygen, which might be ascribed to the great gain of resonance energy in the reaction (5c) ⟶ (6c).

An analogous case in the literature is the thermal conversion of 2*H*-indene (18) into indene (17). Roth[22] found a much higher rate than for the reverse reaction (Scheme 8).



SCHEME 8

The fast [1,5] hydrogen shift in (5c) explains the fact that the occurrence of (5c) as an intermediate could not be demonstrated spectroscopically; this is equally the case for the existence of (5a) in the photocyclization of (4a).[5]

(c) *The formation of* 9-*arylphenanthrenes* (9c). As stated above, the formation of (9c) does take place by oxidation of (5c) in the presence of iodine. As a solution of I_2 in methanol has an absorption at 300 nm, iodine radicals can be formed by direct irradiation. The oxidation of (5c) can then be effected by these iodine radicals.

(d) *The formation of* 1-*phenylphenanthrenes* (10c). Compound (10c) is formed *via* a concerted photocyclization from the S_1 state of *cis*-(4c) into 1-phenyl-4a,4b-dihydrophenanthrene (11c), similar to the photocyclization of *cis*-stilbenes.[18,23] Under non-oxidative conditions this cyclization is completely reversible. The oxidation of (11c) to (10c) can proceed in several ways.[6] In the presence of oxygen the thermal oxidation of (11c) by O_2 is, under the conditions used (see Experimental section), the most probable process. When I_2 is present, the oxidation of (11c) can be effected by iodine radicals as well (see above).

EXPERIMENTAL

Mass spectra were taken with a Varian Mat SM2B mass spectrometer, n.m.r. spectra with Varian HA-100 and Bruker WH-90 instruments, and u.v. spectra with a Cary 15 spectrophotometer. M.p.s were measured on a Leitz microscope and are uncorrected. Elemental analyses were carried out in the Department for Elemental Analysis by Mr. J. Diersmann.

β-*Aryl*-2-*vinylbiphenyls* (4c).—The synthesis of the triphenylphosphonium salt of 2-bromomethylbiphenyl (12) from 2-biphenylcarboxylic acid was carried out by methods described in the literature.[9-11] The Wittig reactions between the various aldehydes (13) and the phosphonium salt (12) were carried out by three different methods (see also Table 1).

Method A_1.[12] To a solution of (12) (0.010 mol) and (13) (0.011 mol) in absolute methanol (50 ml) was added, with stirring, $NaOCH_3$ (0.010 mol). After stirring for 30 min at room temperature the mixture was heated for 1 h at *ca.* 60 °C. Methanol was evaporated on a vacuum rotary evaporator. The resulting oil was extracted twice with toluene, and the toluene fractions were washed with water to remove any basic residue and the dissolved salts. The toluene layer was dried ($MgSO_4$).

Method A_2. This is the same as above, except that dimethylformamide was used as the solvent instead of methanol.

Method B.[24] To a vigorously stirred solution of (12) (0.10 mol) and (13) (0.011 mol) in dichloromethane (25 ml) was added dropwise a 50% NaOH solution (5 ml) in water. The resulting mixture was stirred for 15 min at room temperature. The organic layer was separated and the water layer was washed twice with ether. The combined ethereal layers were added to the dichloromethane solution and dried ($MgSO_4$).

Purification of Products.—The solutions, obtained *via* method A or B, were evaporated and the resulting oily residues were separated by column chromatography on silica gel (Merck; diam. 0.063—0.200 mm), using 1 : 1 toluene–hexane as eluant. The yield of the Wittig reactions, after purification, was 40—90% (see Table 1A). For characterization by physical and spectroscopic data (Table 1) the mixtures of *cis*- and *trans*-(4c) thus obtained were separated by column chromatography on Al_2O_3 (Baker; neutral) using a gradient of hexane and toluene, going from pure hexane to 1 : 1 hexane–toluene. If possible the separated isomers were recrystallized from methanol.

Unresolved *cis–trans* mixtures could be completely converted into the *trans*-isomer by refluxing in CCl_4 with 5 mol % I_2.[25] In preparative irradiations mostly unresolved mixtures were used.

2-(β-*Arylvinyl*)-2′,3′,4′,5′,6′-*pentadeuteriobiphenyls*(14c).—Compounds (14c) were synthesized as shown in Scheme 4. The Grignard reaction between bromopentadeuteriobenzene and 2-methylcyclohexanone and the subsequent dehydration were performed as described for the reaction between *o*-bromotoluene and cyclohexanone.[11] Aromatization with dichlorodicyanoquinone (DDQ) was done by the method of Arnold *et al.*[26] Bromination with *N*-bromosuccinimide (NBS) and the preparation of the triphenylphosphonium salt was carried out according to Campbell and Wang.[11] The Wittig reaction between this phosphonium salt and the respective aromatic aldehydes and the purification of the products was done as described for the non-deuteriated compounds. The ratio between the n.m.r. integrations of the aromatic and ethylenic protons, combined with mass spectral data, proved that no deuterium was lost during the syntheses (see Table 3).

9-*Aryl*-9,10-*dihydrophenanthrenes* (6c).—Preparative irradiations were carried out in a Rayonet photochemical reactor RPR-100, fitted with 300 nm lamps. Qualitative irradiations were carried out in a quartz cuvette, filled with a *ca.* 10^{-5}M solution of (4c) in methanol under nitrogen, using a Philips HPK 125 W lamp.

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[22] W. Roth, *Tetrahedron Letters*, 1964, 1009.

[23] H. Stegemeyer, *Z. Naturforsch.*, 1962, **17b**, 153.

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

[25] W. J. Muizebelt and R. J. F. Nivard, *J. Chem. Soc.* (*B*), 1968, 913.

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

General procedure. A 2 × 10^{-3}M solution of (4c) in methanol was made oxygen free either by boiling the solution and cooling it to room temperature under a gentle stream of oxygen free nitrogen, or by bubbling oxygen free argon through the solution for 30 min. The oxygen free solutions were irradiated in quartz tubes at 300 nm until no further change in the u.v. spectrum occurred [16—20 h, except for the *p*-nitrophenyl derivative (4cvi), when 70 h were necessary]. The mixtures were evaporated *in vacuo*, and the resulting oily residues chromatographed on Al_2O_3, using 4 : 1 hexane–toluene as eluant. The resulting product (6c) was recrystallized from methanol. The yield after purification was 80—90%. The formation of slight amounts (1—2%) of 1-phenylphenanthrenes (10c) is probably due to residual oxygen in the irradiation mixtures.

Quenching and sensitizing experiments. The irradiations with the triplet sensitizers benzil and benzophenone were carried out in a ' merry-go-round ' apparatus, the Rayonet RPR-100, fitted with 350 nm lamps. The concentration of (4ciii and iv) was 10^{-3}M in ethanol and the concentrations of the sensitizers 8 × 10^{-3}, 2 × 10^{-2}, and 4 × 10^{-2}M. The irradiations with the triplet quencher azulene were also carried out in the RPR-100 at 350 nm. The concentration of (4cii and iii) was 10^{-3}M in ethanol and the concentrations of azulene were 10^{-3} and 3 × 10^{-3}M. The results were corrected for the absorption of azulene.

Oxidation of 9-*aryl*-9,10-*dihydrophenanthrenes* (6c) *to* 9-*arylphenanthrenes* (9c). The oxidation of (6ci) to 9ci) and of (6ciii) to (9ciii) was performed in xylene, using DDQ as oxidizing agent.[26] 9-Phenylphenanthrene (9ci) was recrystallized from methanol, m.p. 103.5—104.5 °C (lit.,[27] 104—105 °C). 9-*p*-Methoxyphenylphenanthrene (9ciii) was recrystallized from methanol, m.p. 154—155 °C (lit.,[28] 155.5—156 °C).

[7/1950 *Received*, *7th November*, 1977]

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[27] B. M. Vittimberga, *Tetrahedron Letters*, 1965, 2383.

[28] C. K. Bradsher and R. S. Kittila, *J. Amer. Chem. Soc.*, 1950, **72**, 277.