

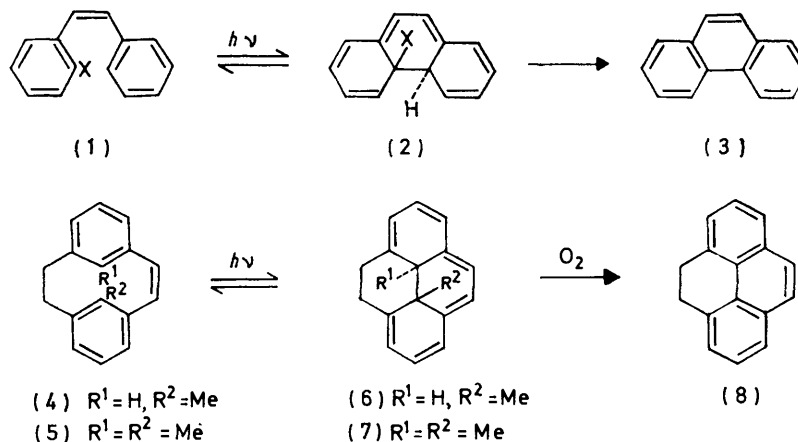
Photochemical Synthesis of Phenanthrenes from 2-Methoxystilbenes¹

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2-Methoxystilbenes undergo photocyclisation to phenanthrenes by a non-oxidative process involving the elimination of methanol.

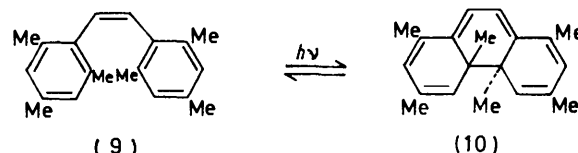
PHOTOCYCLISATION of *cis*-stilbenes to phenanthrenes has been the subject of intensive investigation.² The weight of evidence is that the first excited singlet state of the *cis*-stilbene undergoes orbital symmetry controlled cyclisation to a *trans*-4a,4b-dihydrophenanthrene,^{3,4} which is then oxidised thermally or photochemically by oxygen to the phenanthrene.⁵

group is obscure. However when both points of cyclisation were blocked as in the 1,2-didehydro[2.2]-metacyclophane (5) the intermediate (7) was stable to oxygen. A similar case is the dihydrophenanthrene (10) obtained on photocyclisation of the hexamethylstilbene (9).⁶ It is therefore likely, in view of these results, that the photocyclisation of 2-methylstilbenes and their



A number of examples are known where stilbene photocyclisation occurs by ejection of a substituent at the point of cyclisation. Thus a stilbene with an *ortho*-substituent X (1) would undergo photocyclisation to a *trans*-dihydrophenanthrene (2). The latter could yield phenanthrene (3) by either an oxidation involving oxygen or a non-oxidative elimination process which may well be thermal in nature. Ramsay and Boekelheide³ have shown that the didehydro[2.2]metacyclophane (4) underwent photocyclisation to the tetrahydropyrene (6) which was very sensitive to oxygen and gave 4,5-dihydropyrene (8). The exact fate of the methyl

analogues to yield a phenanthrene by expulsion of the methyl group involves an oxidative process.⁷ The



⁴ T. D. Doyle, N. Filipescu, W. R. Benson, and D. Baner, *J. Amer. Chem. Soc.*, 1970, **92**, 6371.

⁵ A. Bromberg and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1969, **91**, 2860.

⁶ K. A. Muszkat, D. Gegiou, and E. Fischer, *Chem. Comm.*, 1965, 447; K. A. Muszkat and E. Fischer, *J. Chem. Soc. (B)*, 1967, 662.

⁷ P. Bortolus, G. Cauzzo, and G. Galiazzo, *Tetrahedron Letters*, 1966, 239; W. Carruthers and H. N. M. Stewart, *J. Chem. Soc. (C)*, 1967, 556; K. L. Servis and K. N. Fang, *Tetrahedron Letters*, 1968, 967; E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163.

¹ Preliminary communication, R. G. F. Giles and M. V. Sargent, *J.C.S. Chem. Comm.*, 1974, 215.

² E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482.

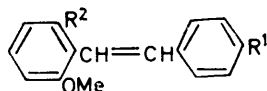
³ C. E. Ramsay and V. Boekelheide, *J. Amer. Chem. Soc.*, 1970, **92**, 3681, and references therein.

cyclisation of 2-chlorostilbene analogues with expulsion of the chloro-substituent, however, appears to fall in the category of a non-oxidative elimination process.⁸

We now describe our results on the photocyclisation of 2-methoxystilbenes. During our work on the synthesis of piloquinone⁹ we observed that u.v. irradiation through Pyrex of cyclohexane solutions of the stilbenes (11), (16), and (17) in the presence of air and iodine gave appreciable yields of methyl phenanthrene-3-carboxylate and the phenanthrenes (19) and (20) respectively, as well as the expected products (32), (22), and (23).

Wood and Mallory¹⁰ reported that u.v. irradiation of 2-methoxystilbene (12) under oxidative conditions gave a detectable amount of phenanthrene (3), which they were unable to isolate, the major product being 1-methoxyphenanthrene (34). In our hands, u.v. irradiation of 2-methoxystilbene (12) in deoxygenated cyclohexane under nitrogen gave phenanthrene (3) as the major product. Similarly when the chlorostilbene⁹ (18) was irradiated under oxidative conditions 3-chloro-1,8-dimethoxy-2-methylphenanthrene (24) was the major product,⁹ and in the absence of oxygen the major product was 3-chloro-1-methoxy-2-methylphenanthrene (21).

In order to determine the scope of this reaction we investigated the u.v. irradiation through silica in the absence of oxygen of the stilbenes (13)—(15) and (25)—(30). The latter were prepared by Wittig reaction between the appropriate aldehyde and phosphonium salt. The products, generally obtained in



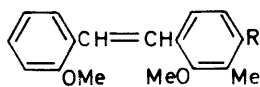
(11) $R^1 = \text{CO}_2\text{Me}, R^2 = \text{H}$

(12) $R^1 = R^2 = \text{H}$

(13) $R^1 = \text{Cl}, R^2 = \text{OMe}$

(14) $R^1 = \text{CO}_2\text{Me}, R^2 = \text{OMe}$

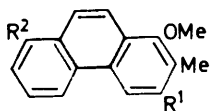
(15) $R^1 = \text{CHMe}_2, R^2 = \text{OMe}$



(16) $R = \text{CO}_2\text{Me}$

(17) $R = \text{CN}$

(18) $R = \text{Cl}$



(19) $R^1 = \text{CO}_2\text{Me}, R^2 = \text{H}$

(20) $R^1 = \text{CN}, R^2 = \text{H}$

(21) $R^1 = \text{Cl}, R^2 = \text{H}$

(22) $R^1 = \text{CO}_2\text{Me}, R^2 = \text{OMe}$

(23) $R^1 = \text{CN}, R^2 = \text{OMe}$

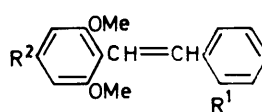
(24) $R^1 = \text{Cl}, R^2 = \text{OMe}$

high yield, of the irradiation of the stilbenes (13)—(15) and (25)—(30) were the phenanthrenes (31)—(39), respectively. The structures of all the new phenanthrenes followed unambiguously from their n.m.r. spectra (see Experimental section).

In all cases except compounds (29) and (30) cyclisation to phenanthrenes could only occur by loss of methanol.

⁸ M. P. Cava, P. Stern, and K. Wakisaka, *Tetrahedron*, 1973, **29**, 2245; M. P. Cava, M. J. Mitchell, S. C. Havlicek, A. Lindert, and R. J. Spangler, *J. Org. Chem.*, 1970, **35**, 175.

With the stilbenes (29) and (30) cyclisation could alternatively lose a methyl group. The only cyclised products detected, (38) and (39), arose by loss of

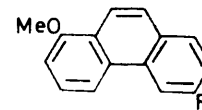


(25) $R^1 = R^2 = \text{H}$

(26) $R^1 = \text{OMe}, R^2 = \text{H}$

(27) $R^1 = \text{H}, R^2 = \text{OMe}$

(28) $R^1 = R^2 = \text{OMe}$

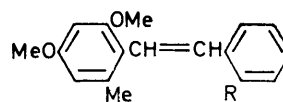


(31) $R = \text{Cl}$

(32) $R = \text{CO}_2\text{Me}$

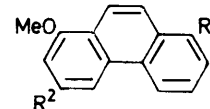
(33) $R = \text{CHMe}_2$

(34) $R = \text{H}$



(29) $R = \text{H}$

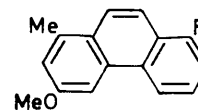
(30) $R = \text{OMe}$



(35) $R^1 = \text{OMe}, R^2 = \text{H}$

(36) $R^1 = \text{H}, R^2 = \text{OMe}$

(37) $R^1 = R^2 = \text{OMe}$



(38) $R = \text{H}$

(39) $R = \text{OMe}$

methanol. This latter observation is in accord with the theory that cyclisation of 2-methylstilbenes with expulsion of a methyl group is an oxidative process whereas the photocyclisation of 2-methoxystilbenes *via* the intermediate (2; X = OMe) is a non-oxidative process involving elimination of methanol. Methanol was detected by g.l.c. in the photolysate obtained from the irradiation of the stilbene (26). The elimination of methanol may be a thermal process.

These results are similar to those obtained by Kanaoka and Itoh¹¹ on the photochemistry of 2-methoxybenz-anilides which cyclise to phenanthridones by a similar elimination of methanol.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage. Light petroleum refers to a fraction b.p. 58—65°. Silica gel was B.D.H. 60—120 mesh material and plates for preparative t.l.c. (p.l.c.) were made from Merck kieselgel GF₂₅₄. I.r. spectra were determined for Nujol mulls using a Perkin-Elmer 337 grating spectrophotometer. N.m.r. spectra were determined at 60 MHz using a Varian A60-A spectrometer or at 90 MHz using a Bruker spectro-spin instrument. For the latter, assignments were assisted by appropriate spin decoupling or INDOR experiments. Mass spectra were determined using a Varian MAT-CH7 instrument operating at 70 eV.

2,6-Dimethoxybenzaldehyde.—Dimethyl sulphate (33 ml) in acetone (50 ml) was added with stirring to a mixture of

⁹ T. M. Cresp, R. G. F. Giles, M. V. Sargent, C. Brown, and D. O'N. Smith, preceding paper.

¹⁰ C. S. Wood and F. B. Mallory, *J. Org. Chem.*, 1964, **29**, 3373.

¹¹ Y. Kanaoka and K. Itoh, *J.C.S. Chem. Comm.*, 1973, 647.

2,6-dimethoxybenzoic acid (52.8 g), potassium carbonate (100 g), and acetone (300 ml). The mixture was then stirred and heated under reflux for 23 h. Work-up in the usual way gave the crude methyl ester (51.4 g). This in dry tetrahydrofuran (200 ml) was added with stirring over 0.75 h to a mixture of lithium aluminium hydride (6 g) and dry tetrahydrofuran (300 ml). The mixture was then stirred and heated under reflux for 1 h and then cooled in ice. Saturated aqueous sodium sulphate was added with stirring until coagulation occurred. The organic layer was separated by filtration and the coagulate was washed with ethyl acetate. The dried (Na_2SO_4) filtrate was evaporated and the crude alcohol (42.7 g) obtained was stirred and heated under reflux (Dean-Stark apparatus) in benzene (500 ml) with activated manganese dioxide¹² (120 g) for 24 h. The manganese dioxide was separated by filtration through kieselguhr and was then washed with hot chloroform. Removal of the solvent gave the aldehyde (37.7 g, 78% overall) which crystallised from dichloromethane–light petroleum as plates, m.p. 96–97° (lit.,¹³ 98–99°), not raised after several recrystallisations.

General Procedure for Preparations of Stilbenes.—Lithium methoxide [from lithium (26 mg atom)] in dry methanol (25 ml) was added dropwise over 1 h to a stirred solution of the phosphonium salt (26 mmol) and the aldehyde (20 mmol) in dry methanol (75 ml) under dry nitrogen at room temperature. The mixture was heated under reflux for 5–10 h and most of the methanol was then removed under reduced pressure. Water was added to the residue which was then extracted with light petroleum. The dried (Na_2SO_4) extract was evaporated and the residue was pre-adsorbed from dichloromethane on silica gel and chromatographed over a column of silica gel with 2.5–5.0% ethyl acetate–light petroleum as eluant. The stilbene was obtained as a mixture of isomers in which the *trans*-isomer predominated. This was purified by crystallisation. The following stilbenes were prepared in this manner.

trans-2-Methoxystilbene (12). This was prepared from 2-methoxybenzaldehyde⁹ and benzyltriphenylphosphonium chloride¹⁴ in 95% yield, needles (from light petroleum), m.p. 66–67° (lit.,¹⁵ 68°), ν_{max} 966 (*trans* CH def.) cm^{-1} .

trans-2,6-Dimethoxystilbene (25).—This was prepared from 2,6-dimethoxybenzaldehyde and benzyltriphenylphosphonium chloride in 40% yield, prisms (from pentane), m.p. 48–50° (Found: C, 79.9; H, 6.4%; M^+ , 240. $\text{C}_{16}\text{H}_{16}\text{O}_2$ requires C, 79.95; H, 6.7%; M , 240), ν_{max} 969 (*trans* CH def.) cm^{-1} .

trans-2,2',6-Trimethoxystilbene (26). This was prepared from 2,6-dimethoxybenzaldehyde and 2-methoxybenzyltriphenylphosphonium chloride⁹ in 59% yield, blades (from methanol), m.p. 94–95° (Found: C, 75.3; H, 7.0. $\text{C}_{17}\text{H}_{18}\text{O}_3$ requires C, 75.55; H, 6.7%; ν_{max} 979 (*trans* CH def.) cm^{-1} .

trans-2,4,6-Trimethoxystilbene (27). This was prepared from 2,4,6-trimethoxybenzaldehyde¹⁶ and benzyltriphenylphosphonium chloride in 77% yield, clusters of prisms (from light petroleum), m.p. 58–59° (Found: C, 75.3; H, 6.65. $\text{C}_{17}\text{H}_{18}\text{O}_3$ requires C, 75.55; H, 6.7%), ν_{max} 980 (*trans* CH def.) cm^{-1} .

trans-2,2',4,6-Tetramethoxystilbene (28). This was prepared in 52% yield from 2,4,6-trimethoxybenzaldehyde and 2-methoxybenzyltriphenylphosphonium chloride, small rods

¹² O. Mancera, G. Rosenkrantz, and F. Sondheimer, *J. Chem. Soc.*, 1954, 5544.

¹³ G. Wittig, *Angew. Chem.*, 1940, **53**, 241.

¹⁴ K. Freidrich and H.-G. Henning, *Chem. Ber.*, 1959, **92**, 2756.

¹⁵ H. Kauffmann, *Annalen*, 1923, **433**, 237.

(from methanol), m.p. 101–102° (Found: C, 72.0; H, 6.8. $\text{C}_{18}\text{H}_{20}\text{O}_4$ requires C, 72.0; H, 6.7%), ν_{max} 983 (*trans* CH def.) cm^{-1} .

trans-2,4-Dimethoxy-6-methylstilbene (29). This was prepared from 2,4-dimethoxy-6-methylbenzaldehyde¹⁶ and benzyltriphenylphosphonium chloride in 90% yield, needles (from cold pentane), m.p. 42–44° (Found: C, 80.35; H, 7.3%; M^+ , 254. $\text{C}_{17}\text{H}_{18}\text{O}_3$ requires C, 80.3; H, 7.15%; M^+ , 254), ν_{max} 966 (*trans* CH def.) cm^{-1} .

trans-2,2',4-Trimethoxy-6-methylstilbene (30). This was prepared from 2,4-dimethoxy-6-methylbenzaldehyde and 2-methoxybenzyltriphenylphosphonium chloride in 63% yield. It crystallised from aqueous methanol as prisms, m.p. 64–66° (Found: C, 75.65; H, 7.4%; M^+ , 284. $\text{C}_{18}\text{H}_{20}\text{O}_3$ requires C, 76.05; H, 7.1%; M , 284), ν_{max} 983 (*trans* CH def.) cm^{-1} .

4'-Chloro-2,6-dimethoxystilbene (13). This was prepared from 2,6-dimethoxybenzaldehyde and 4-chlorobenzyltriphenylphosphonium chloride¹⁷ in 76% yield. It was obtained as an oily mixture of isomers, b.p. 220° (bath) at 0.8 mmHg, *m/e* 276/274 (M^+).

Methyl trans-2',6'-dimethoxystilbene-4-carboxylate (14). This was prepared in 22% yield from 2,6-dimethoxybenzaldehyde and 4-methoxycarbonylbenzyltriphenylphosphonium bromide,⁹ needles (from methanol), m.p. 113–114° (Found: C, 72.8; H, 6.25%; M^+ , 298. $\text{C}_{18}\text{H}_{18}\text{O}_4$ requires C, 72.45; H, 6.1%; M , 298), ν_{max} 1705 (CO) and 977 (*trans* CH def.) cm^{-1} .

trans-4'-Isopropyl-2,6-dimethoxystilbene (15). This was prepared in 38% yield from 4-isopropylbenzyltriphenylphosphonium bromide¹⁸ and 2,6-dimethoxybenzaldehyde, fine needles (from aqueous methanol), m.p. 63–64° (Found: C, 80.85; H, 7.85%; M^+ , 282. $\text{C}_{19}\text{H}_{22}\text{O}_2$ requires C, 80.8; H, 7.85%; M , 282).

General Procedure for Photochemical Reactions.—Cyclohexane (AnalaR) was boiled under reflux with the passage of a stream of dry, oxygen-free nitrogen. It was allowed to cool to room temperature under nitrogen. The stilbene (1.00 g) in deoxygenated cyclohexane (600 ml) was stirred and irradiated for the specified time under oxygen-free nitrogen using a Hanovia 500 W medium pressure mercury lamp with a silica cooling jacket. In this way the following stilbenes were irradiated.

trans-2-Methoxystilbene (12). This was irradiated through Pyrex for 30 h. P.l.c. (light petroleum) gave phenanthrene (3) (58%) and a mixture of *cis*- and *trans*-2-methoxystilbene and 1-methoxyphenanthrene (34) (15%). The latter crystallised from methanol as clusters of needles, m.p. 101–103° (lit.,¹⁹ 105°), τ (60 MHz, CCl_4) 1.45 (1H, m, 5-H), 1.70–2.75 (7H, m, 3-, 4-, 6-, 7-, 8-, 9-, and 10-H), 3.15 (1H, d, $J_{2,3}$ 8.0 Hz, 2-H), and 6.02 (3H, s, OMe).

trans-4-Chloro-2,2'-dimethoxy-3-methylstilbene (18). This was irradiated through Pyrex for 68 h. P.l.c. (light petroleum) afforded 3-chloro-1-methoxy-2-methylphenanthrene (21) (12%), prisms (from aqueous methanol), m.p. 65–67° (Found: C, 74.55; H, 5.1%; M^+ , 258/256. $\text{C}_{16}\text{H}_{13}\text{ClO}$ requires C, 74.85; H, 5.1%; M , 258/256), τ (60 MHz, CCl_4) 1.68 (1H, m, 5-H), 1.72 (1H, s, 4-H), 2.17 and 2.48 (2H, ABq, $J_{9,10}$ 9.0 Hz, 10- and 9-H), 2.25–2.67 (3H, m, 6-, 7-,

¹⁶ I. M. Godfrey, M. V. Sargent, and J. A. Elix, *J.C.S. Perkin I*, 1974, 1353.

¹⁷ R. A. Jones and M.-A. Talmat, *Austral. J. Chem.*, 1965, **18**, 903.

¹⁸ A. P. Bindra, J. A. Elix, and M. V. Sargent, *Austral. J. Chem.*, 1971, **24**, 1721.

¹⁹ L. F. Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 2460.

and 8-H), 6.22 (3H, s, OMe), and 7.56 (3H, s, Me). A mixture of the *cis*- and *trans*-stilbenes (6.5%) and 3-chloro-1,8-dimethoxy-2-methylphenanthrene⁹ (24) (7.0%) was also obtained.

trans-2,6-Dimethoxystilbene (25). This was irradiated for 9 h. Chromatography of the crude product over silica gel with 2.5% ethyl acetate–light petroleum as eluant gave 1-methoxyphenanthrene (34) (90%) identical with that described above.

trans-2,2',6-Trimethoxystilbene (26). This was irradiated for 15 h. The crude product was chromatographed over silica gel with 5% ethyl acetate–light petroleum as eluant. This gave 1,8-dimethoxyphenanthrene (35) (91%), plates (from dichloromethane–light petroleum), m.p. 196–198° (Found: C, 80.3; H, 5.9%; M^+ , 238). $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.9%; M , 238), τ (60 MHz, CCl_4) 1.84 (2H, d, $J_{2,3} = J_{6,7}$ 8.0 Hz, 2- and 7-H), 1.88 (2H, s, 9- and 10-H), 2.56 (2H, dd, $J_{2,3} = J_{3,4} = J_{5,6} = J_{6,7}$ 8.0 Hz, 3- and 6-H), 3.13 (2H, d, $J_{3,4} = J_{5,6}$ 8.0 Hz, 4- and 5-H), and 5.99 (6H, s, OMe). Methanol was detected in the photolysate by g.l.c. and co-g.l.c. [Perkin-Elmer model 880; 5% Carbowax 4000 on 80–100 mesh Chromosorb W column (0.067 in \times 15 ft); column temp. 40°; nitrogen flow rate 26 ml min⁻¹]. Under these conditions methanol had t_R 5.4 min.

trans-2,4,6-Trimethoxystilbene (27). This was irradiated for 48 h. The crude product was chromatographed over silica gel with 5% ethyl acetate–light petroleum as eluant. The product, 1,3-dimethoxyphenanthrene (36) (85%) was obtained as an oil, b.p. 130° (bath) at 0.05 mmHg (Found: C, 80.45; H, 6.25%; M^+ , 238). $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.9%; M , 238), τ (60 MHz, CCl_4) 1.61 (1H, m, 5-H), 1.95 (1H, d, $J_{9,10}$ 9.0 Hz, 10-H), 2.20–2.75 (5H, m, 4-, 6-, 7-, 8-, and 9-H), 3.60 (1H, d, $J_{2,4}$ 2.0 Hz, 2-H), and 6.25 (6H, s, OMe).

trans-2,2',4,6-Tetramethoxystilbene (28). This was irradiated for 39 h. The crude product was chromatographed over silica gel with 2.5% ethyl acetate–light petroleum as eluant. The first material eluted was 1,3,8-trimethoxyphenanthrene (37) (74%, based on unrecovered starting material), which crystallised from dichloromethane–light petroleum as rosettes of needles, m.p. 129–130° (Found: C, 76.3; H, 6.15%; M^+ , 268). $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%; M , 268), τ (90 MHz, CCl_4) 1.98 (1H, d, $J_{5,6}$ 8.0 Hz, 5-H), 2.00 (2H, s, 9- and 10-H), 2.58 (1H, d, $J_{2,4}$ 2.0 Hz, 4-H), 2.66 (1H, dd, $J_{5,6} = J_{6,7}$ 8.0 Hz, 6-H), 3.20 (1H, d, $J_{6,7}$ 8.0 Hz, 7-H), 3.52 (1H, d, $J_{2,4}$ 2.0 Hz, 2-H), and 6.06, 6.07, and 6.10 (each 3H, s, OMe). Later fractions gave the starting material (40%) as a mixture of *cis*- and *trans*-isomers.

trans-2,4-Dimethoxy-6-methylstilbene (29). This was irradiated for 55 h. The crude product was chromatographed over a column of silica gel with 2.5% ethyl acetate–light petroleum as eluant. The first material eluted was 3-methoxy-1-methylphenanthrene (38) (38%, based on unrecovered starting material), which crystallised from methanol as plates, m.p. 89–90° (Found: C, 86.55; H, 6.8; M^+ , 222). $C_{16}H_{14}O$ requires C, 86.45; H, 6.35%; M ,

222), τ (90 MHz, $CDCl_3$) 1.40 (1H, m, 5-H), 2.05–2.50 (6H, m, 4-, 6-, 7-, 8-, 9-, and 10-H), 2.91 (1H, dd, $J_{2,4}$ 2.5, $J_{2,6}$ 0.7 Hz, 2-H), 6.03 (3H, s, OMe), and 8.31 (3H, d, $J_{2,6}$ 0.7 Hz, Me). Later fractions gave the starting material (74%), as a mixture of *cis*- and *trans*-isomers.

trans-2,2',4-Trimethoxy-6-methylstilbene (30). This was irradiated for 42.5 h. The crude product was chromatographed over silica gel with 2.5% ethyl acetate–light petroleum as eluant. The first material eluted was 3,8-dimethoxy-1-methylphenanthrene (39) (63%, based on unrecovered starting material), which crystallised from methanol as glistening plates, m.p. 138–140° (Found: C, 81.1; H, 6.45%; M^+ , 252). $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%; M , 252), τ (90 MHz, $CDCl_3$) 1.83 (1H, d, $J_{5,6}$ 8.0 Hz, 5-H), 1.88 and 2.17 (2H, ABq, $J_{9,10}$ 9.0 Hz, 9- and 10-H), 2.13 (1H, d, $J_{2,4}$ 2.5 Hz, 4-H), 2.51 (1H, dd, $J_{5,6} = J_{6,7}$ 8.0 Hz, 6-H), 2.92 (1H, dd, $J_{2,4}$ 2.5, $J_{2,6}$ 0.7 Hz, 2-H), 3.07 (1H, d, $J_{6,7}$ 8.0 Hz, 7-H), 6.01 and 6.05 (each 3H, s, OMe), and 7.31 (3H, d, $J_{2,6}$ 0.7 Hz, Me). Late fractions gave the starting material (51%) as a mixture of *cis*- and *trans*-isomers.

4'-Chloro-2,6-dimethylstilbene (13). This was irradiated for 11 h. The crude product was crystallised from dichloromethane–light petroleum and gave 6-chloro-1-methoxyphenanthrene (31) (56%) as needles, m.p. 124–125° (Found: C, 74.3; H, 4.65%; M^+ , 244/242). $C_{15}H_{11}ClO$ requires C, 74.25; H, 4.55%; M , 244/242), τ (90 MHz, $CDCl_3$) 1.42 (1H, d, $J_{5,7}$ 2.0 Hz, 5-H), 1.79 and 2.36 (2H, ABq, $J_{9,10}$ 9.0 Hz, 10- and 9-H), 1.88 (1H, d, $J_{3,4}$ 8.0 Hz, 4-H), 2.23 (1H, d, $J_{7,8}$ 8.5 Hz, 8-H), 2.45 (1H, dd, $J_{3,4} = J_{2,3}$ 8.0 Hz, 3-H), 2.50 (1H, dd, $J_{5,7}$ 2.0, $J_{7,8}$ 8.5 Hz, 8-H), 3.03 (1H, d, $J_{2,3}$ 8.0 Hz, 2-H), and 6.01 (3H, s, Me).

Methyl *trans*-2',6'-dimethoxystilbene-4-carboxylate (14). This was irradiated for 46.5 h. P.l.c. (2.5% ethyl acetate–light petroleum) gave methyl 8-methoxyphenanthrene-3-carboxylate (32) (48%, based on unrecovered starting material), needles (from methanol), m.p. 112–113° (lit.⁹ 112–113°), and the starting material (31%) as a mixture of *cis*- and *trans*-isomers.

trans-4'-Isopropyl-2,6-dimethoxystilbene (15). This was irradiated for 14 h. Chromatography of the crude product over silica gel with 5% ethyl acetate–light petroleum as eluant gave 6-isopropyl-1-methoxyphenanthrene (33) (87%) as an oil, b.p. 180° (bath) at 0.8 mmHg (Found: C, 86.1; H, 7.45%; M^+ , 250). $C_{18}H_{18}O$ requires C, 86.35; H, 7.25%; M , 250), τ (60 MHz, CCl_4) 1.62br (1H, s, 5-H), 1.80 (1H, d, $J_{3,4}$ 8.0 Hz, 4-H), 1.90 and 2.41 (2H, ABq, $J_{9,10}$ 9.0 Hz, 10- and 9-H), 2.27 (1H, d, $J_{7,8}$ 8.0 Hz, 8-H), 2.58 (1H, dd, $J_{2,3} = J_{3,4}$ 8.0 Hz, 3-H), 2.63 (1H, d, $J_{7,8}$ 8.0 Hz, 7-H), 3.17 (1H, d, $J_{2,3}$ 8.0 Hz, 2-H), 6.04 (3H, s, OMe), 6.87 (1H, septet, Me_2CH), and 8.62 (6H, d, Me).

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