A New Phenanthrene Synthesis

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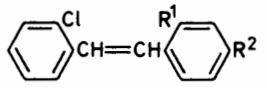
Substituted (*Z*)-2-chlorostilbenes give good yields of phenanthrenes on treatment with activated magnesium formed by the reduction of magnesium chloride with potassium in the presence of potassium iodide in boiling tetrahydrofuran. A homolytic substitution mechanism is proposed for this reaction.

During work designed to synthesize certain natural products [1] it was observed by two of us (C. B. and B. J. S.) that stereoisomeric mixtures of 2-chlorostilbenes on treatment with activated magnesium, obtained by reduction of anhydrous magnesium chloride with potassium in the presence of potassium iodide in boiling tetrahydrofuran (THF) as described by Rieke and Bales,[2] gave phenanthrenes. We now report a more detailed investigation of this reaction.

The 2-chlorostilbenes, except (*Z*)-2-chlorostilbene,[3] were prepared by Wittig reactions carried out by the *in situ* method using *NN*-dimethylformamide (DMF) as solvent. These conditions generally give a preponderance of the (*Z*)-isomer [4] which was easily separated from the (*E*)-isomer by crystallization and distillation, or chromatography. When the (*Z*)-isomers (1)—(6) were treated with the activated magnesium in boiling THF good yields (64—83%) of phenanthrene, the phenanthrenes (7)—(10), and 9-phenylphenanthrene were obtained. It was not possible to extend this method to the synthesis of 9,10-dihydrophenanthrenes; thus no 2,4-dimethoxy-9,10-dihydrophenanthrene could be detected when 2-chloro-3′,5′-dimethoxybibenzyl was treated with activated magnesium. As expected, treatment of (*E*)-2-chlorostilbene with activated magnesium gave no phenanthrene; instead (*E*)-stilbene was obtained.

It has been reported [5] that the Grignard reagents derived from (*Z*)-2-bromostilbenes are converted into phenanthrenes on treatment with cobalt(II) chloride. These conditions are known to produce radicals and it is likely that a similar homolytic substitution occurs in the present case. When 1-bromonaphthalene was heated under reflux for 1 h with activated magnesium and the resultant Grignard reagent was allowed to react with carbon dioxide a 96% isolated yield of 1-naphthoic acid was obtained. However, when 1-chloronaphthalene was treated under the same conditions the products were naphthalene (39%) and 1-naphthoic acid (34%). An involatile gum was also obtained which had signals in its ^{1}H n.m.r. spectrum arising from aromatic protons and at similar chemical shifts to those of the α- and β-protons of THF; it failed to give a mass spectral molecular ion. It is thus likely that chloroarenes react with activated magnesium forming intermediates with a high degree of radical character. Bromoarenes, on the other hand, give normal Grignard reagents. This dichotomy no doubt reflects the different bond energies of the carbon–halogen bonds in the chloro- and bromo-arenes. The yields of Grignard reagents from chloroarenes reported by Rieke and Bales [2] are doubtless overestimated since they were obtained by hydrolysis. In keeping with the above hypothesis an 80% isolated yield of (*E*)-4-methoxystilbene was obtained when (*Z*)-2-bromo-4′-methoxystilbene was treated with activated magnesium, and no 3-methoxyphenanthrene (8) could be detected. It was also observed that the activated magnesium is able to isomerize (*Z*)-stilbene to (*E*)-stilbene. No isomerization was detected when (*Z*)-stilbene was heated under reflux in THF containing magnesium chloride and potassium iodide, the potassium being omitted.



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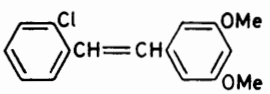
(2) $R^1 = OMe, R^2 = H$
(3) $R^1 = H, R^2 = OMe$



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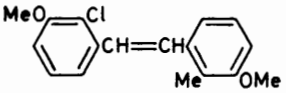

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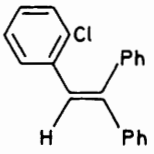

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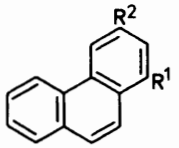
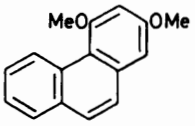


(7) $R^1 = OMe, R^2 = H$
(8) $R^1 = H, R^2 = OMe$



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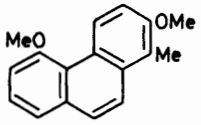

(10)

This method of phenanthrene synthesis is a useful alternative to the photochemical synthesis of phenanthrenes from stilbenes.[6]

Experimental

General directions have been given before.[7] Alumina was Fluka neutral, activity I (Brockmann). Anhydrous magnesium chloride was obtained from the Aldrich Chemical Company. Light petroleum refers to that fraction boiling in the range 58—65 °C. Electronic spectra were determined for solutions in ethanol using a Varian DMS-80 spectrophotometer.

General Procedure for Preparation of Stilbenes by Wittig Reaction.—Lithium methoxide [from lithium (30 mg-atom)] in anhydrous methanol (20 ml) was added dropwise over 2.5 h

under dry nitrogen at 90 °C (bath) to a stirred solution of the phosphonium salt (30 mmol) and the aldehyde (25 mmol) in anhydrous DMF (50 ml). The solution was stirred and heated at 90 °C for a further 1 h, cooled, and poured into water. The mixture was then extracted with ethyl acetate and the extract was washed in turn with water and with saturated brine. The crude products were purified as described below.

2-Chlorostilbene (1). The (*Z*)-isomer was prepared by the method of De Tar and Chu [3] and was obtained as an oil, b.p. 130 °C at 1.5 mmHg (lit.,[3] 118—120 °C at 1.5—2 mmHg); $\lambda_{max.}$ 216(infl.) and 270 nm (ε 17 800 and 9 800). The (*E*)-isomer was obtained by isomerization [3] of the (*Z*)-isomer and had m.p. 38—39 °C (lit.,[3] 39—40 °C); $\lambda_{max.}$ 205, 220(infl.), 227, and 297 nm (ε 21 600, 13 900, 14 600, and 23 800).

2-Chloro-2′-methoxystilbene (2). This was obtained in 95% yield as a 2 : 1 mixture (by ^{1}H n.m.r.) of (*Z*)- and (*E*)-isomers from the Wittig reaction between 2-methoxybenzyltriphenylphosphonium chloride [4] and 2-chlorobenzaldehyde. The crude product was chromatographed over silica gel with light petroleum as eluant to give, first, the (*E*)-isomer as needles (from methanol), m.p. 61.5—62.5 °C (lit.,[8] b.p. 85—90 °C at 0.005 mmHg); δ ($CDCl_3$; 90 MHz) 3.84 (3 H, s, OMe) and 6.81—7.76 (total 10 H, m, 8 × ArH and C*H*=C*H*); $\lambda_{max.}$ 209, 235, 285, and 321 nm (ε 26 400, 15 100, 17 200, and 18 600). Further elution gave the (Z)-*isomer* as plates (from methanol), m.p. 68—69 °C (Found: C, 73.2; H, 5.55; Cl, 14.0%; M^+, 244 and 246. $C_{15}H_{13}ClO$ requires C, 73.6; H, 5.35; Cl, 14.5%; *M*, 244 and 246); δ ($CDCl_3$; 90 MHz) 3.77 (3 H, s, OMe) and 6.56—7.41 (total 10 H, m, 8 × ArH and C*H*=C*H*); $\lambda_{max.}$ 199 and 273 nm (ε 34 900 and 8 700). The (*Z*)-isomer was converted into the (*E*)-isomer on being heated under reflux with a trace of iodine in nitrobenzene.

2-Chloro-4′-methoxystilbene (3). This was obtained in 88% yield as a 1.5 : 1 mixture (by ^{1}H n.m.r.) of (*Z*)- and (*E*)-isomers by the Wittig reaction between 4-methoxybenzyltriphenylphosphonium chloride [9] and 2-chlorobenzaldehyde. The triphenylphosphine oxide was removed by filtration through a plug of silica gel with 10% ethyl acetate–light petroleum as eluant. Most of the (*E*)-isomer was removed by crystallization of the product from methanol, and the (*Z*)-isomer was purified by fractionation of the evaporated mother liquor under reduced pressure. The (*E*)-isomer formed plates (from methanol), m.p. 59—60 °C (lit.,[10] 62—63 °C); δ ($CDCl_3$; 90 MHz) 3.80 (3 H, s, OMe) and 6.85—7.67 (total 10 H, m, 8 × ArH and C*H*=C*H*); $\lambda_{max.}$ 206, 231, and 320 nm (ε 21 000, 13 600, and 24 900). The (Z)-*isomer* was obtained as an oil, b.p. 170 °C (kugelrohr) at 0.5 mmHg (Found: C, 73.4; H, 5.4%; M^+, 244 and 246. $C_{15}H_{13}ClO$ requires C, 73.6; H, 5.35%; *M*, 244 and 246); δ ($CDCl_3$; 90 MHz) 3.69 (3 H, s, OMe), 6.54 and 6.60 (2 H, AB, *J* 12.5 Hz, C*H*=C*H*), and 6.60—7.66 (8 H, m, 8 × ArH); $\lambda_{max.}$ 204(infl.), 231, and 290 nm (ε 27 100, 15 300, and 13 400).

2-Chloro-3′,5′-dimethoxystilbene (4). This was prepared in 85% yield as a 2 : 1 mixture (by ^{1}H n.m.r.) of (*Z*)- and (*E*)-isomers from 3,5-dimethoxybenzyltriphenylphosphonium bromide [11] and 2-chlorobenzaldehyde. The triphenylphosphine oxide was removed by filtration through a plug of silica gel with 2.5% ethyl acetate–light petroleum as eluant. Fractionation of the crude product under diminished pressure gave the (Z)-*isomer* as an oil, b.p. 190 °C (kugelrohr) at 0.1 mmHg (Found: C, 69.75; H, 5.35; Cl, 12.85%; M^+, 274 and 276. $C_{16}H_{15}ClO_2$ requires C, 69.95; H, 5.5; Cl, 12.9%; *M*, 274 and 276); δ ($CDCl_3$; 90 MHz) 3.54 (6 H, s, 2 × OMe), 6.29 (3 H, s, 2′-,4′-, and 6′-H), 6.62 (2 H, s, C*H*=C*H*), and 6.85—7.40 (4 H, ABCD, 3-,4-,5-, and 6-H); $\lambda_{max.}$ 201 and 278 nm (ε 33 000 and 9 700). The (*E*)-isomer was obtained by heating a portion of the mixture with a few crystals of iodine in nitrobenzene under reflux under dry nitrogen for 1 h. The cooled solution was diluted with ethyl acetate and was washed with aqueous sodium thiosulphate. The solvents were removed in steam and the residue was passed through a plug of alumina with 10% ethyl acetate–light petroleum as eluant. The product was then distilled at 205 °C (kugelrohr) at 0.11 mmHg and the distillate was crystallized from cold methanol to give the (E)-*isomer* as needles, m.p. 31—32 °C (Found: C, 70.05; H, 5.6; Cl, 12.9%; M^+, 274 and 276. $C_{16}H_{15}ClO_2$ requires C, 69.95; H, 5.5; Cl, 12.9%; *M*, 274 and 276); δ ($CDCl_3$; 90 MHz) 3.80 (6 H, s, 2 × OMe), 6.40 (1 H, t, *J* 2.25 Hz, 4′-H), 6.67 (2 H, d, *J* 2.25 Hz, 2′- and 6′-H), 6.97 and 7.47 (2 H, AB, *J* 16.0 Hz, C*H*=C*H*), and 7.11—7.68 (4 H, ABCD, 3-,4-,5-, and 6-H); $\lambda_{max.}$ 213, 230(infl.), and 302 nm (ε 28 900, 17 800, and 19 500). A mixture of the isomers (4.4 g) was stirred under hydrogen with 10% palladized charcoal (0.4 g) in ethyl acetate (150 ml) containing concentrated hydrochloric acid (4 drops) until absorption had ceased (0.5 h). The usual work-up gave 1-(2-*chlorophenyl*)-2-(3,5-*dimethoxyphenyl*)*ethane* (4.0 g) as an oil, b.p. 190 °C (kugelrohr) at 0.12 mmHg (Found: C, 69.45; H, 6.2%; M^+, 276 and 278. $C_{16}H_{17}ClO_2$ requires C, 69.45; H, 6.2%; *M*, 276 and 278); δ ($CDCl_3$; 90 MHz) 2.92 (4 H, AA′BB′, 2 × CH_2), 3.73 (6 H, s, 2 × OMe), 6.35 (3 H, narrow m, 3 × ArH), and 7.02—7.37 (4 H, m, 4 × ArH).

2-Chloro-3,3′-dimethoxy-2′-methylstilbene (5). A solution of methyl 3-methoxy-2-methylbenzoate [m.p. 26—28 °C (lit.,[4] b.p. 100—102 °C at 1 mmHg)] (21.5 g) in dry diethyl ether (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (6.8 g) in dry diethyl ether (200 ml). After the addition was complete the mixture was stirred and heated under reflux for 13 h. The ice-cooled mixture was then treated in turn with an excess of water and with dilute hydrochloric acid. Isolation of the product with ethyl acetate in the usual way gave 3-methoxy-2-methylbenzyl alcohol (17.1 g). A sample formed needles (from hexane), m.p. 63—64 °C (lit.,[12] 62—63 °C).

A solution of the alcohol (18.0 g) in anhydrous benzene (150 ml) containing freshly distilled thionyl chloride (28.2 g) and dry pyridine (5 ml) was heated under reflux for 3 h. The cooled solution was then diluted with ethyl acetate and was washed in turn with water, saturated aqueous sodium hydrogen carbonate, water, and lastly with saturated brine. The crude product, on filtration through a plug of alumina with 10% ethyl acetate–light petroleum as eluant, gave 3-methoxy-2-methylbenzyl chloride as a solid (16.7 g). A sample was crystallized from cold, light petroleum and formed needles, m.p. 25—27 °C (lit.,[12] b.p. 30 °C at 0.03 mmHg).

A solution of the chloride (16.0 g) and triphenylphosphine (27.0 g) in dry toluene (100 ml) was heated under reflux under dry nitrogen for 20.5 h. The solution was cooled in ice and prisms (32.2 g) of *3-methoxy-2-methylbenzyltriphenylphosphonium chloride*, m.p. 250—252 °C were separated by filtration and were washed with light petroleum (Found: C, 75.0; H, 6.1; Cl, 7.95. $C_{27}H_{26}ClOP$ requires C, 74.9; H, 6.05, Cl, 8.2%); δ ($CDCl_3$; 90 MHz) 1.46 (3 H, d, $J_{P,Me}$ 1.5 Hz, Me), 3.72 (3 H, s, OMe), 5.25 (2 H, d, J_{P,CH_2} 14.2 Hz, CH_2), 6.63—7.28 (3 H, m, 3 × ArH), and 7.56—7.87 (15 H, m, 3 × Ph).

The title stilbene was prepared in 83% yield from the foregoing phosphonium salt and 2-chloro-3-methoxybenzaldehyde [13] and was obtained as a 1.5 : 1 mixture (by ^{1}H n.m.r.) of (*Z*)- and (*E*)-isomers. The crude product was filtered through a plug of alumina with 10% ethyl acetate–light petroleum as eluant, and was then fractionally crystallized from methanol. The (Z)-*isomer* formed glistening plates, m.p. 115—117 °C (Found: C, 71.05; H, 6.35; Cl, 12.2%; M^+, 288 and 290. $C_{17}H_{17}ClO_2$ requires C, 70.7; H, 5.95; Cl, 12.3%; *M*, 288 and 290); δ ($CDCl_3$; 90 MHz) 2.14 (3 H, s, Me), 3.77 and 3.84 (each 3 H, s, OMe), and 6.49—7.00 (total 8 H, m, 6 × ArH

and C*H*=C*H*); $\lambda_{max.}$ 203, 215, and 270 nm (ε 34 000, 28 100, and 10 500). The (E)-*isomer* formed needles (from methanol), m.p. 154.5—155.5 °C (Found: C, 70.85; H, 5.95; Cl, 12.1%; M^+, 288 and 290. $C_{17}H_{17}ClO_2$ requires C, 70.7; H, 5.95; Cl, 12.3%; *M*, 288 and 290); δ ($CDCl_3$; 90 MHz) 2.29 (3 H, s, Me), 3.81 and 3.87 (each 3 H, s, OMe), and 6.94—7.38 (total 8 H, m, 6 × ArH and C*H*=C*H*); $\lambda_{max.}$ 220 and 297 (ε 17 400 and 16 000).

1-(2-*Chlorophenyl*)-2,2-*diphenylethene* (6). The corresponding Grignard reagent was prepared in the usual way from 2-chlorobenzyl chloride (20.0 g) and magnesium (3.26 g) in dry diethyl ether (250 ml). Benzophenone (24.4 g) in dry diethyl ether (60 ml) was then added to the stirred solution at room temperature during 10 min. The mixture was then heated under reflux for 0.5 h and was then kept overnight. Next day the mixture was stirred and cooled in ice and sulphuric acid (2.5M; 80 ml) was added dropwise. The crude alcohol was isolated with diethyl ether and was immediately distilled under reduced pressure without removal of the remaining sulphuric acid. The distillate, on crystallization from aqueous ethanol, yielded the *ethene* (6) (30.5 g), m.p. 69—71 °C (Found: C, 82.55; H, 5.2%; M^+, 290 and 292. $C_{20}H_{15}Cl$ requires C, 82.6; H, 5.2%; *M*, 290 and 292).

2-*Bromo*-4′-*methoxystilbene*. This was obtained in 95% yield as a 1 : 1 mixture (by ^1H n.m.r.) of stereoisomers from the Wittig reaction between 2-bromobenzyltriphenyl phosphonium bromide [14] and 4-methoxybenzaldehyde. The triphenylphosphine oxide was removed by filtration through a plug of alumina with 10% ethyl acetate–light petroleum as eluant. Crystallization of the product from methanol gave the (E)-*isomer* as glistening plates, m.p. 65—66 °C (Found: C, 62.2; H, 4.6; Br, 27.8%; M^+, 288 and 290. $C_{15}H_{13}BrO$ requires C, 62.3; H, 4.55; Br, 27.65%; *M*, 288 and 290); δ ($CDCl_3$; 90 MHz) 3.80 (3 H, s, OMe) and 6.83—7.67 (total 10 H, m, 8 × ArH and C*H*=C*H*); $\lambda_{max.}$ 206, 232, and 318 nm (ε 24 500, 15 300, and 30 500). Fractionation of the evaporated mother liquor under diminished pressure gave the (*Z*)-isomer as an oil, b.p. 140 °C (kugelrohr) at 0.05 mmHg (lit.,[5] 175—176 °C at 3 mmHg); δ ($CDCl_3$; 90 MHz) 3.72 (3 H, s, OMe), 6.50 and 6.60 (2 H, AB, *J* 12.0 Hz, C*H*=C*H*), and 6.64—7.64 (8 H, m, 8 × ArH); $\lambda_{max.}$ 231 and 283 nm (ε 18 100 and 15 500).

General Procedure for Treatment of Halogenoarenes with Activated Magnesium.—Freshly cut potassium (40 mg-atom) was added under dry nitrogen to a stirred suspension of anhydrous magnesium chloride (20.25 mmol) and anhydrous, finely ground potassium iodide (10 mmol) in freshly distilled, anhydrous THF (50 ml) in a flame-dried apparatus. The mixture was heated under reflux under dry nitrogen for 3 h and a solution of the halogenoarene (10 mmol) in dry THF (20 ml) was added during 0.5 h to the stirred and heated suspension. The mixture was then heated and stirred under reflux for 12 h. The stirred mixture was cooled in ice and then water was added dropwise under dry nitrogen. The crude product was isolated with ethyl acetate in the usual way and was usually subjected to g.c.–m.s. analysis using a Hewlett-Packard 5986 system with a 0.31 mm i.d. × 25 m OV-101 wall coated open tubular capillary column and helium as carrier gas. The following reagents were used.

(Z)-2-*Chlorostilbene* (1). Analysis of the crude product by g.c.–m.s. indicated that (*E*)-stilbene comprised 6.8% of the total ion current and phenanthrene comprised 72.7%. The crude product was filtered through a plug of alumina with light petroleum as eluant, and crystallization from methanol then gave phenanthrene (83%) as plates, m.p. 98—100 °C, identical (mixed m.p., n.m.r. and mass spectra) with an authentic sample).

(Z)-2-*Chloro*-2′-*methoxystilbene* (2). The crude product was filtered through a plug of alumina with light petroleum as eluant. 1-Methoxyphenanthrene (7) (76%) crystallized from methanol as needles, m.p. 102—103 °C (lit.,[15] 105 °C); δ ($CDCl_3$; 90 MHz) 3.96 (3 H, s, OMe), 6.89 (1 H, d, $J_{2,3}$ 7.5 Hz, 2-H), 7.46 and 8.22 (2 H, AB, $J_{9,10}$ 9.0 Hz, 9- and 10-H), 7.52—7.90 (4 H, m, 3-,6-,7-, and 8-H), 8.22 (1 H, d, $J_{3,4}$ 9.0 Hz, 4-H), and 8.66—8.68 (1 H, m, 5-H); $\lambda_{max.}$ 214, 223(infl.), 254, 293, 305, 319, 335, and 351 nm (ε 25 500, 23 000, 25 200, 10 000, 10 700, 1 700, 2 300, and 2 600).

(Z)-2-*Chloro*-4′-*methoxystilbene* (3). The crude product was filtered through a plug of alumina with light petroleum as eluant. Analysis of the oily product by g.c.–m.s. indicated that (*E*)-4-methoxystilbene comprised 9.0% of the total ion current and 3-methoxyphenanthrene (8) comprised 83.3%. Fractional crystallization of this material gave crude (*E*)-4-methoxystilbene (10%) as plates (from methanol), m.p. 125—132 °C (lit.,[16] 136 °C). The crude 3-methoxyphenanthrene obtained from the mother liquor was distilled at 140 °C (kugelrohr) at 0.11 mmHg, and the distillate was crystallized from methanol, whereupon it formed plates of 3-methoxyphenanthrene (8) (77%), m.p. 57—58 °C (lit.,[5] 57—58 °C); δ ($CDCl_3$; 90 MHz) 3.95 (3 H, s, OMe), 7.14—8.01 (8 H, m, 8 × ArH), and 8.51—8.61 (1 H, m, 4-H); $\lambda_{max.}$ 228, 250, 274, 289(infl.), 302, 319(infl.), 337, and 353.5 nm (ε 40 500, 35 800, 14 500, 8 600, 10 100, 2 000, 2 100, and 1 700).

(Z)-2-*Chloro*-3′,5′-*dimethoxystilbene* (4). Analysis of the crude product by g.c.–m.s. showed that 2,4-dimethoxyphenanthrene (9) comprised 77.9% of the total ion current. The crude product was filtered through a plug of alumina with 2.5% ethyl acetate–light petroleum as eluant and the oily product was distilled at 190 °C (kugelrohr) at 0.11 mmHg and was then crystallized from methanol as needles of 2,4-dimethoxyphenanthrene (9) (64%), m.p. 76.5—78 °C (lit.,[17] 75.5—76.5 °C) (Found: C, 80.7; H, 5.95%; M^+, 238. Calc. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.9%; *M*, 238); δ ($CDCl_3$; 90 MHz) 6.72 and 6.82 (2 H, AB, $J_{1,3}$ 2.5 Hz, 3-, and 1-H), 7.37—7.86 (5 H, m, 6-, 7-, 8-, 9-, and 10-H), and 9.47—9.57 (1 H, m, 5-H); $\lambda_{max.}$ 219, 223, 226, 256, 278(infl.), 288(infl.), 299(infl.), 339, and 355 nm (ε 20 100, 19 100, 18 300, 23 100, 14 600, 10 400, 7 000, 1 400, and 1 800).

(Z)-2-*Chloro*-3,3′-*dimethoxy*-2′-*methylstilbene* (5). Crystallization of the crude product from methanol gave needles of 2,5-*dimethoxy*-1-*methylphenanthrene* (10) (76%), m.p. 120—122 °C (Found: C, 81.05; H, 6.35%; M^+, 252. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%; *M*, 252); δ ($CDCl_3$; 100 MHz) 2.54 (3 H, s, Me), 3.84 (3 H, s, 2-OMe), 3.95 (3 H, s, 5-OMe), 6.97 (1 H, X part of ABX, 6-H), 7.30 and 7.40 (2 H, AB part of ABX, 7- and 8-H), 7.58 and 7.84 (2 H, AB, $J_{9,10}$ 9.0 Hz, 9- and 10-H), and 7.18 and 9.54 (2 H, AX, $J_{3,4}$ 9.0 Hz, 3- and 4-H) (saturation of the methoxy-group signal at δ 3.95 gave a 13% nuclear Overhauser effect at the 6-H signal); $\lambda_{max.}$ 212, 236(infl.), 260, 279, 286(infl.), 296(infl.), 310, 318, 347, and 363 nm (ε 22 200, 13 000, 45 400, 25 200, 17 300, 11 200, 10 500, 1 000, 1 200, and 1 200).

1-(2-*Chlorophenyl*)-2,2-*diphenylethene* (6). The ethene was added in a thin stream at 0 °C and the mixture was then stirred at room temperature for 12 h. The crude product was crystallized from aqueous ethanol as needles of 9-phenylphenanthrene (71%), m.p. 104—105 °C (lit.,[18] 105—106 °C) (Found: C, 94.8; H, 5.4%; M^+, 254. Calc. for $C_{20}H_{14}$: C, 94.45; H, 5.55%; *M*, 254); $\lambda_{max.}$ 209, 212, 248(infl.), 255, 285(infl.), 296, 325(infl.), 333, 341, and 350 nm (ε 34 000, 34 000, 48 500, 57 500, 11 000, 13 500, 400, 390, 280, and 320).

(E)-2-*Chlorostilbene* (1). The stilbene (5.00 g) gave a crude product which was filtered through a plug of alumina with 5% ethyl acetate–light petroleum as eluant. Crystallization of the product from methanol then gave (*E*)-stilbene (1.75 g). The evaporated residue was distilled at 155 °C (kugelrohr) at

0.3 mmHg to give more (*E*)-stilbene which formed needles (from methanol) (total 2.03 g), m.p. 123—124 °C (lit.,[19] 124 °C), and an involatile residue (0.97 g).

1-*Bromonaphthalene*. The freshly distilled naphthalene (5.00 g) was heated under reflux with activated magnesium for 1 h in the usual way. Dry carbon dioxide was then passed through the mixture for 4.5 h at such a rate that the temperature did not exceed −3 °C. No naphthalene could be detected in the crude product by either t.l.c. or g.c–m.s. The usual work-up gave 1-naphthoic acid as needles (4.00 g, 96%) (from ethanol), m.p. 161.5—162.5 °C (lit.,[20] 162 °C).

1-*Chloronaphthalene*. This compound (5.00 g) was treated in the same way as 1-bromonaphthalene. The crude product, in diethyl ether, was extracted with aqueous sodium hydrogen carbonate in the usual way. Work-up then gave crude 1-naphthoic acid (2.22 g) which, on crystallization from ethanol, formed needles (1.81 g, 34%), m.p. 161.5—162.5 °C. The neutral portion was sublimed onto a cold finger at 50 °C and 760 mmHg; this gave naphthalene as plates (1.52 g, 39%), m.p. and mixed m.p. 79.5—80.5 °C, and an involatile gum (0.70 g).

(Z)-2-*Bromo*-4′-*methoxystilbene*. The crude product was crystallized from methanol and formed plates (80%) of (*E*)-4-methoxystilbene, m.p. 134—135 °C (lit.,[16] 136 °C); $\lambda_{max.}$ 203, 229, 302, and 317 nm (ε 22 000, 12 900, 26 100, and 25 300).

(Z)-*Stilbene*. Work-up after 0.5 h gave a quantitative yield of (*E*)-stilbene as needles, m.p. 124—125 °C (from methanol). No isomerization occurred when the potassium was omitted from the reaction.

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