

Synthesis of Chrysenes and Other α -Fused Phenanthrenes by a Palladium(0) Coupling—Electrocyclic Ring Closure Sequence¹

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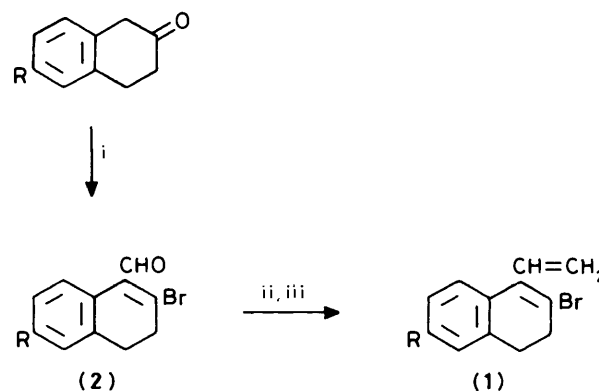
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2-Bromo-1-vinyl-3,4-dihydronaphthalene (**1a**) has been coupled with several vinyl-, aryl-, and heteroaryl-zinc halides in the presence of tetrakis(triphenylphosphine)palladium(0) to give the corresponding 2-vinyl-, 2-aryl-, and 2-heteroaryl-naphthalenes in good yield. These compounds, which can be regarded as conjugated trienes, undergo electrocyclic ring closure when heated in solution. In the case of the cyclopentenone derivative (**5a**) this cyclisation is preceded by a [1,7] hydrogen shift. Some related reactions are described starting from the 6-methoxy derivative (**1b**) of compound (**1a**). The coupling reaction has also been carried out with 2-bromo-3,4-dihydronaphthalene-1-carbaldehyde (**2a**) and with the acetals (**2c**) and (**2d**). An alternative method of cyclisation has been explored which involves the bromine-lithium exchange reaction of compound (**1a**) and of the isomeric bromo-naphthalene (**3b**), followed by reaction with ketones and acid-catalysed dehydration. The polycyclic hydrocarbons (**11**) and (**14**) have been prepared by this method.

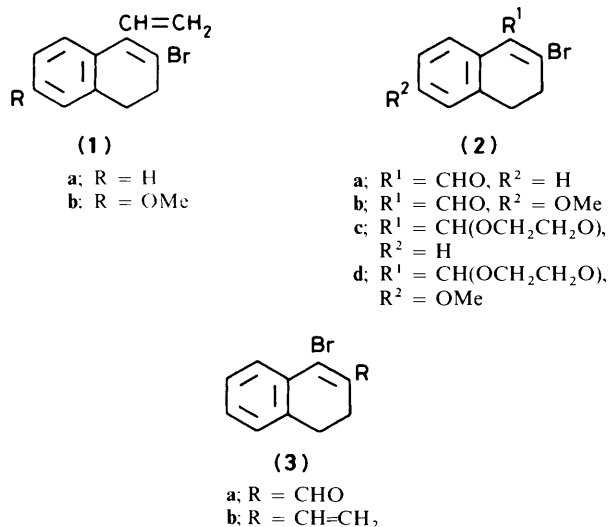
In an earlier paper we described the preparation of some 2-substituted 1-vinyl-3,4-dihydronaphthalenes and their thermal electrocyclic ring closure.² The usefulness of these reactions was, however, limited by the method used to prepare the substituted naphthalenes, which allowed the preparation of only a restricted range of these compounds in moderate yield. In this paper we describe a more general and more efficient method for their preparation. When combined with their electrocyclic ring closure, which is generally a clean reaction, this provides a method of synthesis of a number of polycyclic aromatic and heteroaromatic compounds which cannot easily be prepared by existing methods.

In recent years the cross coupling of vinyl or aryl halides in the presence of a palladium(0) catalyst has become an important method of formation of carbon-carbon bonds.³ We have used this method to prepare unsaturated compounds suitable for the electrocyclic ring-closure reaction. Because of our interest in using the method to prepare aromatic steroids^{1,2} most of these coupling reactions have been carried out on 2-bromo-1-vinyl-3,4-dihydronaphthalene (**1a**) and on related compounds.

The bromo diene (**1a**) was prepared from 3,4-dihydronaphthalen-2(1*H*)-one in two steps and in an overall yield of 71% by the procedure shown in Scheme 1. Reaction of the

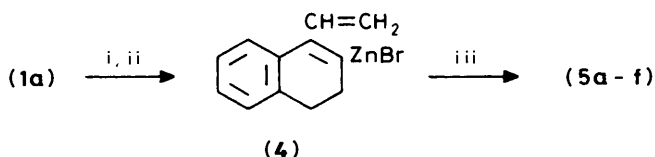


Scheme 1. Reagents: i, PBr_3 , DMF; ii, $\text{Me}_3\text{SiCH}_2\text{MgCl}$; iii, SOCl_2



ketone with phosphorus tribromide and *NN*-dimethylformamide gave the bromoaldehyde (**2a**), which was converted into the diene (**1a**) by a Peterson reaction. By an analogous series of reactions the bromo diene (**1b**) was prepared from 6-methoxy-3,4-dihydronaphthalene-2(1*H*)-one, and compound (**3b**) from 3,4-dihydronaphthalene-1(2*H*)-one. All three bromo dienes were obtained as distillable oils which could be stored for short periods in the refrigerator.

Cross coupling reactions of vinylic halides are normally carried out by the conversion of one component into a suitable organometallic derivative followed by the addition of a catalytic amount of a soluble palladium(0) catalyst and the second halide. Organozinc and organotin reagents appeared, from published work, to be the most suitable. The first successful couplings were achieved by conversion of the bromo diene (**1a**) into the bromozinc intermediate (**4**) by reaction with butyllithium at -78°C followed by the addition of zinc bromide at -20°C . After the addition of a vinyl or aryl iodide and 4 mol % $[\text{Pd}(\text{PPh}_3)_4]$ the coupled products (**5a-f**) were isolated in yields of 47–69% (Scheme 2).

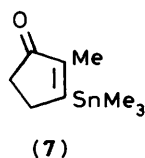


Scheme 2. Reagents: i, BuLi; ii, ZnBr₂; iii, [Pd(PPh₃)₄], R¹Br or R¹I

Coupling was also achieved using the bromo diene (**1a**) as the electrophilic component. Thus, furan was converted into a 2-bromozinc intermediate and this was coupled to compound (**1a**) to give the 2-furylnaphthalene (**5g**) in 72% yield. Compound (**5f**) (72%) could also be prepared by this method, starting from thiophene. One advantage of this 'inverse' coupling procedure is that it allows coupling reactions to be carried out with other 2-bromonaphthalenes, including those with functional groups at the 1-position. Thus, the bromozinc intermediate derived from thiophene was successfully coupled not only to (**1a**), but also to the 6-methoxy derivative (**1b**), to the bromo aldehyde (**2a**), and to the acetals (**2c**) and (**2d**). Compound (**1b**) gave the thienyl-naphthalene (**5h**); corresponding derivatives (**6**) were obtained from reactions of compounds (**2**). Phenylzinc bromide and (**1b**) gave the 2-phenylnaphthalene (**5i**). Yields of products isolated from these reactions were between 44 and 77%, the lowest yield being obtained from the aldehyde (**2a**). This inverse coupling procedure proved useful, because none of these compounds could be successfully coupled by way of their bromozinc derivatives. For example, the bromo diene (**1b**) gave a debrominated compound, 6-methoxy-1-vinyl-3,4-dihydronaphthalene (**5k**), as the major product when coupling reactions were attempted by way of its bromozinc derivative.



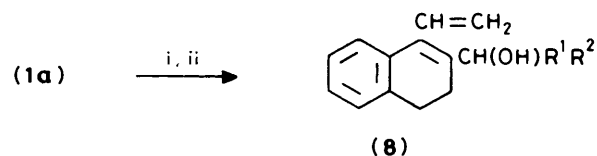
- a: R¹ = 2-methyl-1-oxocyclopent-2-en-3-yl, R² = H
 b: R¹ = 1-oxocyclohex-2-en-3-yl, R² = H
 c: R¹ = (*E*)-2-phenylvinyl, R² = H
 d: R¹ = Ph, R² = H
 e: R¹ = 1-naphthyl, R² = H
 f: R¹ = 2-thienyl, R² = H
 g: R¹ = 2-furyl, R² = H
 h: R¹ = 2-thienyl, R² = OMe
 i: R¹ = Ph, R² = OMe
 j: R¹ = SnMe₃, R² = H
 k: R¹ = H, R² = OMe
- a: R¹ = CHO, R² = H
 b: R¹ = CHO, R² = OMe
 c: R¹ = CH(OCH₂CH₂O), R² = H
 d: R¹ = CH(OCH₂CH₂O), R² = OMe



Organotin species have been used extensively in cross coupling reactions and they have the advantage over organozinc intermediates of being isolable and capable of full characterisation.^{3c} We therefore also investigated coupling reactions of appropriate organotin compounds. The attempted reactions were, however, completely unsuccessful. Thus, the bromo diene

(**1a**) was converted, by reaction with butyl-lithium and chlorotrimethyltin, into the stannane (**5j**), which was isolated as a distillable oil. This failed to react with 3-iodo-2-methylcyclopent-2-enone in the presence of [Pd(PPh₃)₄], even when heated. An inverse coupling using the known⁴ stannane (**7**) and the bromo diene (**1a**) or the bromo aldehyde (**2a**) also failed, the stannane proving too unreactive. With this series of compounds, coupling by way of organozinc intermediates is the better method.

Compounds suitable for electrocycloisatation were also prepared from the bromo diene (**1a**) and simple ketones by way of the organolithium species derived from (**1a**) and butyl-lithium. The vinyl-lithium reagent reacted with cyclopentanone, cyclohexanone, and acetophenone to give the tertiary alcohols (**8a-c**) in good yield (Scheme 3). This reaction was, however, limited



Scheme 3. Reagents: i, BuLi, ii, R¹R²CO

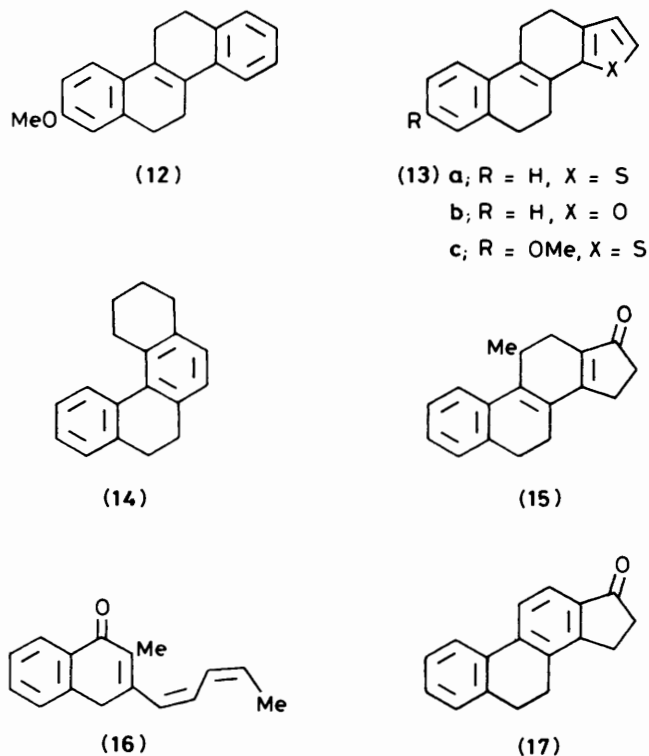
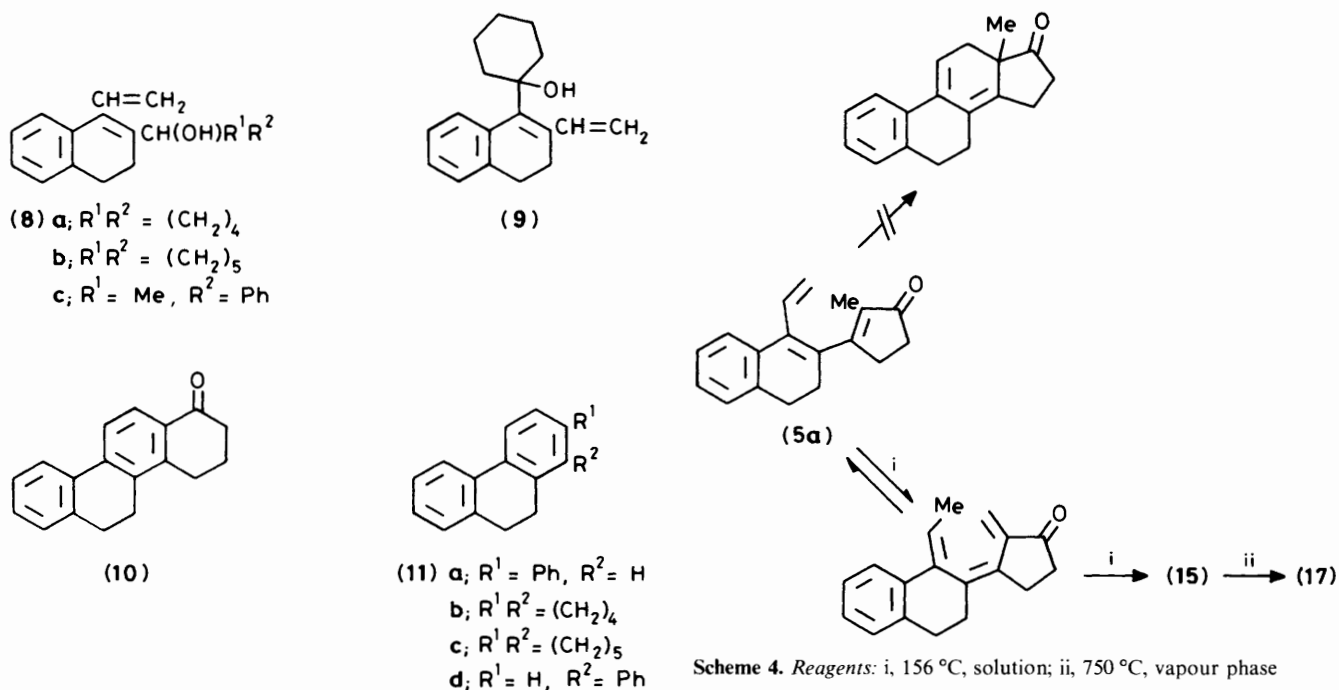
in its scope; in particular, no addition was observed to the unsaturated ketone 3-methoxy-2-methylcyclopent-2-enone. An analogous reaction of the bromo diene (**3b**) with butyl-lithium and cyclohexanone gave the tertiary alcohol (**9**).

Electrocyclic ring closure of the products of the palladium-catalysed coupling reactions was most efficiently achieved by heating them in solution under nitrogen at temperatures in the range 139–180 °C. Compounds (**5b**) and (**5c**) both cyclised readily but the cyclisation was followed by dehydrogenation, the products isolated being the ketone (**10**) and the phenanthrene (**11a**), respectively. 1-Vinyl-3,4-dihydronaphthalenes with an aryl or heteroaryl substituent at the 2-position cyclised without dehydrogenation to give the tetrahydrochrysenes (**12**) [from (**5i**)] and the fused heterocycles (**13**) [from (**5f**), (**5g**), and (**5h**)].

The tertiary alcohols (**8**) and (**9**) were dehydrated and cyclised in a 'one-pot' process by heating them in toluene with a catalytic amount of toluene-*p*-sulphonic acid. The products isolated were the hydrocarbons (**11b-d**) and (**14**).

The trienone (**5a**) did not cyclise in the expected manner. When the compound was heated in bromobenzene at reflux for 24 h it gave a new, isomeric ketone which was isolated in moderate yield. The ¹H n.m.r. spectrum of the ketone was consistent with structure (**15**), the signal for the methyl group appearing as a doublet (*J* 7.1 Hz) at δ 1.02. This compound could be formed by the route shown in Scheme 4 involving a [1,7] hydrogen shift before ring closure. There are several literature analogies for [1,7] shifts preceding cyclisation, including a reaction of the trienone (**16**).⁵ The ring closure of the trienone (**5a**) was also attempted in the vapour phase, the vapour being passed at low pressure through a tube heated at 750 °C. The product, which was isolated in good yield, was the aromatised ketone (**17**). This compound could be formed by the elimination of methane, at the high reaction temperature, from the ketone (**15**). When the vapour phase pyrolysis was attempted at a lower temperature (550 °C) the trienone (**5a**) passed through the hot tube unchanged.

In summary, we have illustrated the versatility of the palladium(0)-catalysed coupling reaction as a procedure for linking unsaturated carbon atoms bearing a wide range of substituents. We have also found that trienes in which the central double bond is part of a ring system can, with a few exceptions, be cyclised efficiently by heating them in solution.



Experimental

M.p.s were recorded on a Reichert hot-stage apparatus and are uncorrected. B.p.s refer to bath temperatures for distillations carried out on a Kugelrohr apparatus. 1H and ^{13}C N.m.r. spectra were recorded on a Bruker WM250 spectrometer, operating at 250 MHz or 62.9 MHz respectively. 1H N.m.r. spectra were also recorded on a Perkin-Elmer R34 instrument, operating at 220 MHz. $CDCl_3$ was used as solvent. Mass spectra were recorded on a VG Micromass 7070E instrument

and are electron impact spectra except where indicated otherwise. Flash column chromatography was carried out using Merck 9385 silica gel and air line pressure. Medium pressure liquid chromatography was carried out using a Gilson 303 pump, a Gilson 803C pressure module, a Rheodyne 7125 injector fitted with a 5 ml loop, and Omnifit columns packed with Merck 15111 silica gel. Tetrahydrofuran (THF) and diethyl ether (ether) were freshly distilled under N_2 from sodium-benzophenone ketyl before use. *N,N*-Dimethylformamide (DMF) was dried by azeotropic removal of water, using benzene, followed by rapid distillation at reduced pressure from activated alumina; it was stored over type 4A molecular sieves under N_2 . Commercial butyl-lithium was estimated by the Gilman double titration method⁶ before use. Petroleum refers to light petroleum, fraction b.p. 40–60 °C.

The following starting materials and reagents were prepared by literature routes: tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$],⁶ 6-methoxy-3,4-dihydronaphthalen-2(1*H*)-one (6-methoxy-2-tetralone),⁷ 3-iodo-2-methyl-cyclopent-2-enone,⁸ 3-iodocyclohex-2-enone,⁹ 2-methyl-3-trimethylstannylcyclopent-2-enone (7),⁴ and β -iodostyrene.¹⁰ 3,4-Dihydronaphthalene-1(2*H*)-one and -2(1*H*)-one were used as supplied commercially.

2-Bromo-3,4-dihydronaphthalene-1-carbaldehyde (2a).—Dry DMF (1.5 g, 20.5 mmol) was cooled to 0 °C in dry chloroform (30 ml) and phosphorus tribromide (1.63 ml, 17.1 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h to give a yellow suspension. A solution of 3,4-dihydronaphthalen-2(1*H*)-one (1.0 g, 6.84 mmol) in chloroform was then added and the mixture heated under reflux for 1 h. It was then allowed to cool to 0 °C when aqueous sodium hydrogen carbonate was slowly added until the effervescence had subsided. The mixture was extracted with dichloromethane and the extract dried and evaporated to give a yellow oil. Flash column chromatography of this using ether-petroleum (1:4) as eluant gave the *aldehyde* (2a) (1.37 g, 84%) as a yellow oil which solidified on cooling, m.p. 26–27 °C (from ethanol) (Found: C, 55.75; H, 3.8. $C_{11}H_9BrO$ requires C, 55.7; H, 3.8%; ν_{max} (Nujol) 1680 cm^{-1} ; δ (220 MHz) 2.75–2.90 (2 H, m), 2.90–3.00 (2 H, m), 7.10–7.15

(1 H, m), 7.20–7.30 (2 H, m), 8.00 (1 H, t), and 10.22 (1 H); m/z 235.9659 [M^+], $C_{11}H_9^{81}BrO$ requires 235.9659], 235, 234, 233, 208, 206, and 126.

2-Bromo-6-methoxy-3,4-dihydronaphthalene-1-carbaldehyde (2b).—6-Methoxy-3,4-dihydronaphthalen-2(1H)-one⁷ (0.50 g, 2.8 mmol) was added to dry DMF (0.61 g, 8.4 mmol) and phosphorus tribromide (0.67 ml, 7.0 mmol) and the mixture was heated under reflux for 1 h. Work-up followed by flash column chromatography gave [with ether–petroleum (1:4)] the aldehyde (**2b**) (1.20 g, 61%) as a pale green solid, m.p. 51–55 °C (from ethanol) (Found: C, 53.8; H, 4.1. $C_{12}H_{11}BrO_2$ requires C, 53.9; H, 4.15%; ν_{max} (Nujol) 1 670 cm^{-1} ; δ (250 MHz) 2.83 (2 H, t), 2.93 (2 H, t), 3.75 (3 H), 6.65 (1 H, d), 6.73 (1 H, dd), 7.95 (1 H, d), and 10.25 (1 H); m/z 268 (M^+).

2-Bromo-1-vinyl-3,4-dihydronaphthalene (1a).—(Trimethylsilyl)methylmagnesium chloride was generated from chloromethyltrimethylsilane (0.57 ml, 4.2 mmol) and magnesium turnings (0.10 g, 4.2 mmol) in THF (5 ml). 2-Bromo-3,4-dihydronaphthalene-1-carbaldehyde (**2a**) (1.0 g, 4.2 mmol) was then added dropwise in THF (10 ml) and the mixture was stirred for 1 h. It was then cooled to 0 °C and thionyl chloride (0.38 ml, 5.2 mmol) slowly added; the mixture was then stirred for a further 1 h. Work-up followed by drying and evaporation gave a brown oil which was purified by flash column chromatography using ether–petroleum (1:9) as eluant, which gave 2-bromo-1-vinyl-3,4-dihydronaphthalene (**1a**) (0.42 g, 85%) as a yellow oil, b.p. 155 °C at 0.1 mmHg (Found: C, 61.6; H, 4.7. $C_{12}H_9Br$ requires C, 61.3; H, 4.7%; δ (250 MHz) 2.60–2.71 (4 H, m), 5.50 (2 H, m, ABX), 6.67 (1 H, dd, ABX), 6.97–7.01 (3 H, m), and 7.24–7.26 (1 H, m); J_{AX} 11.7 Hz, J_{BX} 18.0 Hz, and J_{AB} 1.43 Hz; m/z 236 and 234 (M^+) and 155.

2-Bromo-6-methoxy-1-vinyl-3,4-dihydronaphthalene (1b).—2-Bromo-6-methoxy-3,4-dihydronaphthalene-1-carbaldehyde (**2b**) (3.5 g, 13.8 mmol) was treated with (trimethylsilyl)methylmagnesium chloride (15.0 mmol) in THF for 1 h. Thionyl chloride (1.4 ml, 15.0 mmol) was then added to the mixture at 0 °C. After the mixture had been stirred for 1 h it was subjected to flash column chromatography, the column being eluted with ether–petroleum (1:4). This gave 2-bromo-6-methoxy-1-vinyl-3,4-dihydronaphthalene (**1b**) (3.2 g, 80%) as a pale yellow oil, b.p. 170 °C at 0.1 mmHg (Found: m/z 266.0119. $C_{13}H_{13}^{81}BrO$ requires 266.0129; δ (220 MHz) 2.95 (4 H, br), 3.90 (3 H), 5.60 (2 H, dd), 6.85 (3 H, m), and 7.50 (1 H, d); δ_C 30.54 (t), 35.94 (t), 55.80 (q), 111.46 (d), 114.30 (d), 120.55 (t), 121.40 (s), 127.42 (s), 127.62 (s), 135.02 (d), 137.98 (s), and 159.21 (s).

1-Bromo-3,4-dihydronaphthalene-2-carbaldehyde (3a).—3,4-Dihydronaphthalen-1(2H)-one (1.0 g, 6.84 mmol) was treated with DMF (1.5 g, 20.5 mmol) and phosphorus tribromide (1.63 ml, 17.1 mmol) under reflux for 1 h. Work-up gave the aldehyde (**3a**) (1.24 g, 76%) as a yellow solid, m.p. 42–44 °C (from ethanol) (Found: C, 55.45; H, 3.8. $C_{11}H_9BrO$ requires C, 55.7; H, 3.8%; ν_{max} (Nujol) 1 663 cm^{-1} ; δ (220 MHz) 2.55 (2 H, t), 2.75 (2 H, t), 7.15 (1 H, d), 7.30 (2 H, q), 7.85 (1 H, d), and 10.18 (1 H); m/z 238 and 235.9839 [M^+], $C_{11}H_9^{79}BrO$ requires 235.9836], 237, 235, 209, 207, and 128.

1-Bromo-2-vinyl-3,4-dihydronaphthalene (3b).—1-Bromo-3,4-dihydronaphthalene-2-carbaldehyde (**3a**) (2.5 g, 10.5 mmol) was treated with (trimethylsilyl)methylmagnesium chloride (12.5 mmol) in THF (10 ml) for 1 h. The solution was cooled to 0 °C and thionyl chloride (1.2 ml, 12.5 mmol) was added. After 1 h the reaction mixture was quenched and the product was isolated by flash column chromatography, eluting with ether–petroleum, to give 1-bromo-2-vinyl-3,4-dihydronaphthalene

(**3b**) (2.07 g, 83%) as a yellow oil, b.p. 165 °C at 0.1 mmHg (Found: m/z 234.0009. $C_{12}H_{11}^{79}Br$ requires 234.0086); δ (220 MHz) 2.55 (2 H, t), 2.75 (2 H, t), 5.40 (2 H, dd, ABX), 7.00–7.20 (4 H, m), and 7.50 (1 H, d).

2-Bromo-3,4-dihydronaphthalene-1-carbaldehyde Ethylene Acetal (2c).—The aldehyde (**2a**) (0.5 g, 2.1 mmol) and ethylene glycol (0.14 g, 2.3 mmol) were heated in toluene (150 ml) with a few crystals of toluene-*p*-sulphonic acid under N_2 for 5 h. Flash column chromatography gave [with ether–petroleum (1:4)] the acetal (**2c**) (0.43 g, 73%) (Found: C, 55.5; H, 4.7. $C_{13}H_{13}BrO_2$ requires C, 55.5; H, 4.65%; δ (250 MHz) 2.84 (4 H), 4.04–4.12 (2 H, m), 4.18–4.23 (2 H, m), 6.09 (1 H), 7.08–7.17 (3 H, m), and 7.55 (1 H, dd).

2-Bromo-6-methoxy-3,4-dihydronaphthalene-1-carbaldehyde Ethylene Acetal (2d).—Using a procedure analogous to that for the acetal (**2c**), the aldehyde (**2b**) (1.80 g, 6.74 mmol) was converted into the acetal (**2d**) (1.29 g, 61%), m.p. 115–116 °C (from petroleum) (Found: C, 53.8; H, 4.8. $C_{14}H_{15}BrO_3$ requires C, 54.0; H, 4.85%; δ (220 MHz) 2.81 (4 H), 3.78 (3 H), 3.97–4.10 (2 H, m), 4.15–4.28 (2 H, m), 6.10 (1 H), 6.65–6.75 (2 H, m), and 7.52 (1 H, d).

2-(1-Hydroxycyclopentyl)-1-vinyl-3,4-dihydronaphthalene (8a).—2-Bromo-1-vinyl-3,4-dihydronaphthalene (**1a**) (0.50 g, 2.1 mmol) was treated with butyl-lithium (1.6M; 1.45 ml, 2.3 mmol) in THF (15 ml) at –78 °C for 10 min, followed by cyclopentanone (0.17 ml, 2.1 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 0.5 h before being quenched. Flash chromatography gave [with ether–petroleum (1:7)] the alcohol (**8a**) (0.41 g, 81%) as a yellow oil, b.p. 196 °C at 0.2 mmHg (Found: m/z 240.157. $C_{17}H_{20}O$ requires m/z 240.151); δ (250 MHz) 1.48–1.91 (8 H, m), 2.09 (2 H, dt), 2.31 (1 H, exchanges with D_2O), 2.52 (2 H, t), 5.13 (2 H, ddd, ABX), 6.84–7.00 (4 H, m), and 7.08–7.12 (1 H, m); J_{AX} 11.4 Hz, J_{BX} 18.0 Hz, and J_{AB} 1.9 Hz.

2-(1-Hydroxycyclohexyl)-1-vinyl-3,4-dihydronaphthalene (8b).—2-Bromo-1-vinyl-3,4-dihydronaphthalene (**1a**) (0.50 g, 2.1 mmol) was treated with butyl-lithium (1.4M; 1.5 ml, 2.1 mmol) in THF (15 ml) at –78 °C for 10 min. Cyclohexanone (0.24 ml, 2.3 mmol) was added and the mixture was stirred at –78 °C for 30 min and then at 20 °C for 1 h. Work-up followed by flash column chromatography eluting with ether–petroleum (1:4) gave the alcohol (**8b**) (0.38 g, 71%) as a yellow oil (Found: C, 84.95; H, 8.7. $C_{18}H_{22}O$ requires C, 85.0; H, 8.7%; ν_{max} (film) 3 460 cm^{-1} ; δ (250 MHz) 1.41–1.78 (10 H, m), 2.16–2.22 (2 H, td), 2.33 (1 H, exchanges with D_2O), 2.60 (2 H, t), 5.21 (2 H, ddd, ABX), 7.00–7.17 (4 H, m), and 7.18–7.21 (1 H, m); J_{AX} 13.0 Hz, J_{BX} 19.8 Hz, and J_{AB} 2.3 Hz; m/z 254.166 [M^+], $C_{18}H_{22}O$ requires 254.167], 236, 211, 197, 193, and 179.

2-(1-Hydroxy-1-phenylethyl)-1-vinyl-3,4-dihydronaphthalene (8c).—2-Bromo-1-vinyl-3,4-dihydronaphthalene (**1a**) (0.5 g, 2.1 mmol) was treated with butyl-lithium (1.6M; 1.45 ml, 2.3 mmol) followed by acetophenone (0.5 g, 2.12 mmol). Work-up followed by flash column chromatography gave [with ether–petroleum (1:3)] the alcohol (**8c**) (0.41 g, 71%) as a yellow oil (Found: m/z 276.149. $C_{20}H_{20}O$ requires m/z 276.151); δ (250 MHz) 1.75 (3 H), 2.12–2.35 (2 H, m), 2.62 (2 H, t), 3.00 (1 H, exchanges with D_2O), 5.23 (2 H, ddd, ABX), 6.76 (1 H, dd, ABX), 7.07–7.14 (3 H, m), 7.21–7.32 (4 H, m), and 7.43–7.48 (2 H, m); J_{AX} 11.2 Hz, J_{BX} 18.0 Hz, and J_{AB} 2.1 Hz.

1-(1-Hydroxycyclohexyl)-2-vinyl-3,4-dihydronaphthalene (9).—1-Bromo-2-vinyl-3,4-dihydronaphthalene (**3b**) (1.0 g, 4.2 mmol) was treated with butyl-lithium (4.8 mmol) in THF (45

ml) at -78°C , followed by cyclohexanone (0.42 ml, 4.3 mmol). The reaction mixture was stirred at room temperature for 1 h and then quenched to give (by flash chromatography) the alcohol (**9**) (0.86 g, 81%), as yellow crystals, m.p. $84\text{--}85^{\circ}\text{C}$ (from ether-petroleum) (Found: C, 85.1; H, 8.8. $\text{C}_{18}\text{H}_{22}\text{O}$ requires C, 85.0; H, 8.7%); δ 1.50 (1 H, exchanges with D_2O), 1.60–1.81 (8 H, m), 2.25–2.32 (4 H, m), 2.56 (2 H, t), 5.20 (2 H, ddd, ABX), 7.00–7.18 (3 H, m), and 7.41–7.57 (2 H, m); m/z 254 (M^+).

Coupling Reactions of Bromo(1-vinyl-3,4-dihydro-2-naphthyl)-zinc (4): General Procedure.—A solution of zinc bromide was prepared by heating zinc powder (0.15 g, 2.4 mmol) and 1,2-dibromoethane (0.20 ml, 2.4 mmol) in THF (20 ml) under reflux for 3.5 h. The bromo compound (**1a**) (0.38 g, 1.6 mmol) was allowed to react with butyl-lithium (2.0 mmol) at -78°C and the zinc bromide solution was then added under N_2 . The reaction mixture was stirred at -20°C for 1 h and $[\text{Pd}(\text{PPh}_3)_4]^6$ (70 mg, 4 mol %) and the appropriate halide were added together in THF (25 ml). The mixture was then stirred at room temperature for 16 h. It was quenched with aqueous ammonium chloride and the organic products were extracted with ether. The extracts were dried and evaporated and the residue was purified by flash chromatography, using ether-petroleum (1:1) as the eluant. This general procedure was used to prepare the following compounds:

(a) 2-(2-Methyl-1-oxocyclopent-2-en-3-yl)-1-vinyl-3,4-dihydronaphthalene (**5a**) (50%) (from 3-iodo-2-methylcyclopent-2-enone⁸), b.p. 220°C at 0.1 mmHg (Found: C, 86.5; H, 7.4. $\text{C}_{18}\text{H}_{18}\text{O}$ requires C, 86.4; 7.2%); ν_{max} (film) 1690 cm^{-1} ; δ (250 MHz) 1.66 (3 H), 2.40 (2 H, t), 2.45–2.49 (2 H, m), 2.65–2.71 (2 H, m), 2.80 (2 H, t), 5.32 (2 H, m, ABX), 6.33 (1 H, dd, ABX), 7.20–7.25 (3 H, m), and 7.47–7.51 (1 H, m); m/z 250 (M^+), 235, 207, 194, 193, and 178.

(b) 2-(1-Oxocyclohex-2-en-3-yl)-1-vinyl-3,4-dihydronaphthalene (**5b**) (63%) (from 3-iodocyclohex-2-enone⁹), b.p. 195°C at 0.1 mmHg (Found: m/z 250.136. $\text{C}_{18}\text{H}_{18}\text{O}$ requires m/z 250.135); ν_{max} (film) 1670 cm^{-1} ; δ (220 MHz) 2.05 (2 H, t), 2.45 (2 H, t), 2.50–2.60 (4 H, m), 2.90 (2 H, t), 5.50 (2 H, dd, ABX), 5.94 (1 H), 6.82 (1 H, dd, ABX), 7.15–7.25 (3 H, m), and 7.45 (1 H, d).

(c) 2-[(E)-2-Phenylvinyl]-1-vinyl-3,4-dihydronaphthalene (**5c**) (48%) (from β -iodostyrene¹⁰), m.p. $41\text{--}42^{\circ}\text{C}$ (from petroleum) (Found: C, 93.15; H, 7.0. $\text{C}_{20}\text{H}_{18}$ requires C, 93.0; H, 7.0%); δ (250 MHz) 2.64 (2 H, t), 2.84 (2 H, t), 5.52 (2 H, ddd, ABX), 6.38 (1 H, d, J 16.3 Hz), 6.69 (1 H, dd, ABX), 7.04 (1 H, d, J 16.3 Hz), and 7.10–7.40 (9 H, m); J_{AX} 10.8 Hz, J_{BX} 17.1 Hz, and J_{AB} 2.2 Hz; m/z 298 (M^+).

(d) 2-Phenyl-1-vinyl-3,4-dihydronaphthalene (**5d**) (47%) (from iodobenzene), b.p. 150°C at 0.2 mmHg.²

(e) 2-(1-Naphthyl)-1-vinyl-3,4-dihydronaphthalene (**5e**) (69%) (from 1-iodonaphthalene), b.p. 250°C at 0.1 mmHg (Found: C, 94.0; H, 6.0. $\text{C}_{22}\text{H}_{18}$ requires C, 93.6; H, 6.4%); δ (250 MHz) 2.65–2.87 (2 H, m), 3.11–3.20 (2 H, m), 5.39 (2 H, ddd, ABX), 6.52 (1 H, dd, ABX), 7.36–7.50 (4 H, m), 7.70–7.99 (3 H, m), 7.87 (1 H, dd), 8.03 (1 H, d), and 8.11 (2 H, dd); J_{AX} 11.3 Hz, J_{BX} 17.8 Hz, and J_{AB} 1.7 Hz; m/z 282 (M^+) and 280.

(f) 2-(2-Thienyl)-1-vinyl-3,4-dihydronaphthalene (**5f**) (60%) (from 2-iodothiophene), m.p. 52°C (from ethyl acetate-petroleum) (Found: C, 80.6; H, 6.3. $\text{C}_{16}\text{H}_{14}\text{S}$ requires C, 80.6; H, 5.9%); δ (250 MHz) 2.57 (2 H, m), 2.62–2.69 (2 H, m), 5.29 (2 H, m, ABX), 6.54 (1 H, dd, ABX), 6.83 (1 H, dd, J 5.1 and 3.7 Hz), 6.95–7.02 (4 H, m), 7.08 (1 H, dd, J 5.1 and 1.0 Hz), and 7.34–7.37 (1 H, m); m/z 238 (M^+).

Coupling Reactions with Bromonaphthalenes (1) and (2) as Electrophiles.—(a) 2-(2-Furyl)-1-vinyl-3,4-dihydronaphthalene (**5g**). Furan (0.13 g, 2.0 mmol) was treated with butyl-lithium (2.0 mmol) and TMEDA (2.0 mmol) in ether (15 ml) for 30 min.

The solution was cooled to -20°C and a solution of zinc bromide (3.0 mmol) in THF (20 ml) was added. The reaction mixture was stirred for 1 h and the bromonaphthalene (**1a**) (0.47 g, 2.0 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (0.1 g, 4 mol %) were added together. The mixture was heated under reflux for 2 h. Flash chromatography followed by distillation gave the furan (**5g**) (0.32 g, 72%) as an unstable oil, b.p. 170°C at 0.1 mmHg (Found: m/z 222.1037. $\text{C}_{16}\text{H}_{14}\text{O}$ requires m/z 222.1045); δ (250 MHz) 2.58–2.64 (2 H, m), 2.69–2.75 (2 H, m), 5.36 (2 H, ddd, ABX), 6.36 (1 H, dd, J 3.4 and 1.8 Hz), 6.45 (1 H, d, J 3.4 Hz), 6.84 (1 H, dd, ABX), 7.07–7.15 (3 H, m), 7.34 (1 H, d, J 1.8 Hz), and 7.46–7.50 (1 H, m); J_{AX} 11.3 Hz, J_{BX} 17.9 Hz, and J_{AB} 1.9 Hz.

(b) 6-Methoxy-2-(2-thienyl)-1-vinyl-3,4-dihydronaphthalene (**5h**). 2-Thienyl-lithium (3.0 mmol) was prepared from thiophene (3.0 mmol), butyl-lithium (3.0 mmol), and TMEDA (3.0 mmol) in ether (15 ml) at room temperature. The solution was cooled to -20°C and zinc bromide (3.87 mmol) in THF was added. After 1 h the bromonaphthalene (**1b**) (0.76 g, 2.9 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (0.13 g, 4 mol %) were added in THF (10 ml). The reaction mixture was heated under reflux for 2.5 h. The product was isolated by flash chromatography [ether-petroleum (1:19)] and was identified as the thiophene (**5h**) (0.45 g, 58%), m.p. $64\text{--}65^{\circ}\text{C}$ (from ethyl acetate-petroleum) (Found: C, 75.9; H, 6.2. $\text{C}_{17}\text{H}_{16}\text{OS}$ requires C, 76.1; H, 6.0%); δ (250 MHz) 2.70–2.75 (2 H, m), 2.79–2.86 (2 H, m), 3.82 (3 H), 5.46 (2 H, ABX), 6.69–6.75 (2 H, m), 6.83 (1 H, dd, ABX), 7.02 (1 H, dd, J 5.0 and 3.6 Hz), 7.14 (1 H, d, J 3.6 Hz), 7.25 (1 H, d), and 7.46 (1 H, d); J_{AX} 11.5 Hz, J_{BX} 17.8 Hz, and J_{AB} 1.9 Hz; m/z 268 (M^+), 253, and 235.

6-Methoxy-2-phenyl-1-vinyl-3,4-dihydronaphthalene (**5i**). Zinc bromide (10.0 mmol) in THF was added to phenyl-lithium (8.0 mmol) in ether at -20°C and the mixture was stirred for 1 h. The bromonaphthalene (**1b**) (2.0 g, 7.5 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (0.7 g, 4 mol %) in THF were added and the reaction mixture was heated under reflux for 2.5 h. Flash chromatography gave [with ether-petroleum (1:19)] the naphthalene (**5i**) (1.45 g, 69%), m.p. $43\text{--}45^{\circ}\text{C}$ (from petroleum) (Found: C, 86.9; H, 6.9. $\text{C}_{19}\text{H}_{18}\text{O}$ requires C, 87.0; H, 6.9%); δ (250 MHz) 2.61 (2 H, t), 2.82 (2 H, t), 3.83 (3 H), 5.20 (2 H, ddd, ABX), 6.52 (1 H, dd, ABX), 6.71–6.77 (2 H, m), 7.22–7.34 (5 H, m), and 7.49 (1 H, d); J_{AX} 11.3 Hz, J_{BX} 18.0 Hz, and J_{AB} 2.0 Hz; m/z 282 (M^+), 247, and 231.

2-(2-Thienyl)-2,4-dihydronaphthalene-1-carbaldehyde (**6a**). This compound was prepared using the same procedure as described for the thiophene (**5h**), from 2-thienyl-lithium (6.0 mmol) and the aldehyde (**2a**) (5.9 mmol). Flash chromatography gave [with ether-petroleum (1:4)] the aldehyde (**6a**) (0.63 g, 44%), m.p. $86\text{--}87^{\circ}\text{C}$ (from ethyl acetate-petroleum) (Found: C, 74.8; H, 5.0. $\text{C}_{15}\text{H}_{12}\text{OS}$ requires C, 75.0; H, 5.0%); δ (250 MHz) 2.85–2.92 (4 H, m), 7.10–7.29 (6 H, m), 7.55 (1 H, d, J 5.0 Hz), 8.20–8.23 (1 H, m), and 10.00 (1 H); m/z 240 (M^+), 211, 178, and 165.

2-(2-Thienyl)-3,4-dihydronaphthalene-1-carbaldehyde ethylene acetal (**6c**). This was prepared by the same procedure as for compound (**5h**), from 2-thienyl-lithium (6.0 mmol) and the acetal (**2c**). Flash chromatography gave [with ether-petroleum (1:4)] the acetal (**6c**) (1.29 g, 79%), m.p. $112\text{--}114^{\circ}\text{C}$ (from ether-petroleum) (Found: C, 72.0; H, 5.7. $\text{C}_{17}\text{H}_{16}\text{O}_2\text{S}$ requires C, 71.8; H, 5.7%); δ (250 MHz) 2.65–2.69 (2 H, m), 2.85 (2 H, t), 3.93–4.01 (2 H, m), 4.19–4.25 (2 H, m), 5.78 (1 H), 7.03 (1 H, dd, J 5.0 and 3.3 Hz), 7.14–7.24 (4 H, m), 7.37 (1 H, dd, J 5.0 and 0.9 Hz), and 7.64–7.67 (1 H, m); m/z 284 (M^+), 212, and 178.

6-Methoxy-2-(2-thienyl)-3,4-dihydronaphthalene-1-carbaldehyde ethylene acetal (**6d**). This was prepared by the procedure described for the thiophene (**5h**), from 2-thienyl-lithium (11.9 mmol) and the acetal (**2d**) (11.9 mmol). Flash chromatography gave [with ether-petroleum (1:4)] the acetal (**6d**) (2.9 g, 77%) as

a yellow oil (Found: m/z 314.0971. $C_{18}H_{18}O_3S$ requires m/z 314.0977); δ (250 MHz) 2.61 (2 H, t), 2.78 (2 H, t), 3.74 (3 H), 3.88 (2 H, t), 4.15 (2 H, t), 5.75 (1 H), 6.69–7.10 (2 H, m), 6.96–7.00 (1 H, m), 7.17 (1 H, d, J 3.6 Hz), 7.30 (1 H, d, J 5.0 Hz), and 7.59 (1 H, d, J 8.1 Hz).

Hydrolysis of the acetal (**6d**) (1.0 g, 3.18 mmol) by heating under reflux in 50% aqueous THF (60 ml) with toluene-*p*-sulphonic acid (100 mg) gave the aldehyde (**6c**) (0.79 g, 92%), m.p. 170 °C (from petroleum) (Found: m/z 270.0710. $C_{16}H_{14}O_2S$ requires m/z 270.0714); ν_{max} (Nujol) 1 670 cm^{-1} (C=O); δ (250 MHz) 2.85 (4 H, br), 3.80 (3 H), 6.73–6.80 (2 H, m), 7.06–7.12 (2 H, m), 7.50 (1 H, d), 8.15 (1 H, dd), and 9.95 (1 H).

2-Trimethylstannyl-1-vinyl-3,4-dihydronaphthalene (5i).—The naphthalene (**1a**) (1.0 g, 4.5 mmol) in THF (45 ml) was treated with butyl-lithium (4.7 mmol) at –78 °C. After 10 min chlorotrimethyltin (0.84 g, 4.25 mmol) in THF (5 ml) was added. The mixture was stirred at 10 °C for 0.5 h and then at 20 °C for 4 h. Flash chromatography [with ether–petroleum (1:3)] followed by Kugelrohr distillation gave the stannane (**5j**) (0.45 g, 35%) as an oil, b.p. 205 °C at 0.2 mmHg [Found: m/z (chemical ionisation) 320. $C_{15}H_{20}Sn$ requires m/z 319 (M^+)]; δ (250 MHz) 0.31 (9 H), 2.40 (2 H, t), 2.68 (2 H, t), 5.33 (2 H, ddd, *ABX*), 6.65 (1 H, dd, *ABX*), 7.21–7.30 (3 H, m), and 7.40 (1 H, d); J_{AX} 10.9 Hz, J_{BX} 17.4 Hz, and J_{AB} 2.0 Hz. This compound was not characterised further.

Attempted Coupling Reactions of Stannanes.—(a) *With 2-methyl-3-trimethylstannylcyclopent-2-enone (7)*. Compound (**7**)⁴ (0.2 g, 0.77 mmol) and the bromonaphthalene (**1a**) (0.18 g, 0.77 mmol) were heated in toluene (50 ml) under reflux with [Pd(PPh₃)₄] (35 mg, 11 mol %). After 36 h the solvent was removed; the residue, a yellow oil, contained mainly the starting materials together with a minor component which was isolated but not identified.

Compound (**7**) also failed to react with the bromoaldehyde (**2a**) under similar conditions.

(b) *With the stannane (5h)*. Compound (**5h**) (0.12 g, 0.37 mmol) and 3-iodo-2-methylcyclopent-2-enone (0.08 g, 0.37 mmol) were stirred in THF (25 ml) with [Pd(PPh₃)₄] (20 mg, 4 mol %) for 1.5 h after which the reaction mixture was heated under reflux for 6 h. Only the starting materials could be detected by t.l.c. An attempted reaction carried out in toluene at reflux also gave no detectable products, and a further attempt to bring about the reaction in xylene at reflux led to extensive decomposition of the starting materials.

Thermal Cyclisations: General Procedure.—The reactions were carried out by heating the substrates in dry, degassed xylene or dry, degassed bromobenzene under reflux and under N₂, until none of the starting materials could be detected by t.l.c. [In the cases of the naphthalenes (**5g**), (**5h**), and (**5i**) 1,2-dichlorobenzene was used since no reaction took place in the lower boiling solvents.] The solvent was then removed under reduced pressure and the products were isolated and purified as indicated.

(a) *3,4,5,6-Tetrahydrochrysen-1(2H)-one (10)*. The ketone (**5b**) (0.3 g, 1.2 mmol) was heated in bromobenzene (30 ml) for 32 h. The product, which was isolated by flash chromatography (with ether as eluant) was identified as the ketone (**10**) (0.18 g, 60%), b.p. 100 °C at 0.15 mmHg (Found: m/z 248.119. $C_{18}H_{16}O$ requires m/z 248.120); ν_{max} (film) 1 690 cm^{-1} (C=O); δ (220 MHz) 1.90–2.01 (2 H, m), 2.35–2.60 (4 H, m), 2.85–2.95 (2 H, m), 7.10 (1 H, d), 7.20–7.33 (2 H, m), 7.40–7.50 (1 H, m), 7.60 (1 H, d), and 7.95 (1 H, d).

(b) *2-Phenyl-9,10-dihydrophenanthrene (11a)*. The triene (**5c**) was heated in xylene (35 ml) for 26 h. Flash chromatography

gave [with ether–petroleum (1:19)] the phenanthrene (**11a**) (0.10 g, 67%), m.p. 80–81 °C (from petroleum) (Found: C, 93.65; H, 6.2. $C_{20}H_{16}$ requires C, 93.7; H, 6.3%); δ (220 MHz) 2.85 (2 H, t), 3.05 (2 H, t), 7.10–7.30 (5 H, m), 7.55 (2 H, d), 7.65 (1 H), 7.70 (2 H, d), and 7.90 (2 H, d); m/z 256.124 (M^+ ; $C_{20}H_{16}$ requires m/z 256.125), 204, and 202.

(c) *2-Methoxy-5,6,11,12-tetrahydrochrysen-12-ene (12)*. The naphthalene (**5i**) (0.40 g, 1.52 mmol) was heated in 1,2-dichlorobenzene (70 ml) for 72 h. Flash chromatography gave [with ether–petroleum (2:25)] the chrysen-12-ene (**12**) (0.29 g, 72%), m.p. 83–84 °C (from petroleum) (Found: C, 86.7; H, 6.9. $C_{19}H_{18}O$ requires C, 87.0; H, 6.9%); δ (250 MHz) 2.46 (4 H, t), 2.87 (4 H, t), 3.80 (3 H), 6.71–6.75 (2 H, m), and 7.11–7.30 (5 H, m); m/z 268.091 (M^+ , $C_{19}H_{18}O$ requires m/z 268.092), 266, 253, and 221.

(d) *4,5,10,11-Tetrahydrophenanthro[1,2-b]thiophene (13a)*. The thiophene (**5f**) (0.15 g, 0.63 mmol) was heated in xylene (30 ml) for 32 h. After removal of the solvent the residue partly solidified. It was triturated with petroleum, filtered, and crystallised to give the thiophene (**13a**) (0.11 g, 73%), m.p. 82 °C (from ethyl acetate–petroleum) (Found: C, 80.85; H, 6.0. $C_{16}H_{14}S$ requires C, 80.6; H, 5.9%); δ (250 MHz) 2.57–2.63 (2 H, m), 2.73–2.82 (2 H, m), 2.86–2.95 (2 H, m), 2.99–3.10 (2 H, m), 7.11–7.45 (5 H, m), and 7.78–7.84 (1 H, m); m/z 238 (M^+) and 149.

(e) *4,5,10,11-Tetrahydrophenanthro[1,2-b]furan (13b)*. The furan (**5g**) (0.40 g, 1.8 mmol) was heated in 1,2-dichlorobenzene (65 ml) for 20 h. Flash chromatography gave [with ether–petroleum (1:50)] the furan (**13b**) (0.31 g, 77%), m.p. 97–100 °C (Found: m/z 222.1046. $C_{16}H_{14}O$ requires m/z 222.1045); δ (250 MHz) 2.41 (2 H, t), 2.54 (4 H), 2.62 (2 H, t), 6.10 (1 H, d, J 1.8 Hz), 6.87–7.05 (4 H, m), and 7.08 (1 H, d, J 1.8 Hz).

(f) *8-Methoxy-4,5,10,11-tetrahydrophenanthro[1,2-b]thiophene (13c)*. The thiophene (**5h**) (0.20 g, 0.74 mmol) was heated in 1,2-dichlorobenzene (70 ml) for 48 h. Flash chromatography gave [with ether–petroleum (1:19)] the thiophene (**13c**) (0.15 g, 76%), m.p. 75–77 °C (from ethyl acetate–petroleum) (Found: C, 76.2; H, 5.9. $C_{17}H_{16}OS$ requires C, 76.1; H, 6.0%); δ (250 MHz) 2.56–2.61 (2 H, m), 2.74–2.78 (2 H, m), 2.84–2.92 (4 H, m), 3.82 (3 H), 6.74–6.77 (2 H, m), 6.91 (1 H, d, J 4.8 Hz), 7.08 (1 H, d, J 4.8 Hz), and 7.26 (1 H); m/z 268 (M^+), 266, and 253.

(g) *11-Methyl-6,7,11,12,15,16-Hexahydro-17H-cyclopenta[a]phenanthren-17-one (15)*. The trienone (**5a**) (0.10 g, 0.40 mmol) was heated in bromobenzene (30 ml) for 24 h. Medium pressure chromatography gave (with chloroform) an oil (42 mg, 42%) to which the ketone structure (**15**) was assigned (Found: m/z 250. $C_{18}H_{18}O$ requires m/z 250); ν_{max} (film) 1 680 cm^{-1} (C=O); δ (250 MHz) 1.02 (3 H, d, J 7.1 Hz, 11-Me), 2.45–2.57 (6 H, m), 2.63–2.79 (2 H, m), 2.81–2.88 (2 H, m), 3.15–3.21 (1 H, m, 11-H), 7.17–7.29 (3 H, m), and 7.44 (1 H, d).

6,7,15,16-Tetrahydro-17H-cyclopenta[a]phenanthren-17-one (17) by Flash Vacuum Pyrolysis of the Ketone (5a).—The trienone (**5a**) (85 mg, 0.34 mmol) was distilled at 0.03 mmHg during 1.5 h through a tube heated at 750 °C. The pyrolysate was collected on a cooled surface at the exit of the tube. Crystallisation gave the ketone (**17**) (61 mg, 76%) as a yellow solid, m.p. 102–104 °C (from ether–petroleum) (Found: C, 87.1; H, 6.1. $C_{17}H_{14}O$ requires C, 87.15; H, 6.0%); ν_{max} (Nujol) 1 705 cm^{-1} ; δ (250 MHz) 2.35–2.50 (4 H, m), 2.85–2.90 (4 H, m), 7.05–7.25 (5 H, m), and 7.45–7.55 (1 H, m); m/z 234.1039 (M^+ , $C_{17}H_{14}O$ requires m/z 234.1044), 191, and 131.

Dehydrative Cyclisation of the Alcohols (8) and (9): General Procedure.—The alcohol was heated in toluene under reflux with a few crystals of toluene-*p*-sulphonic acid, for the times stated. The solution was cooled, washed with aqueous sodium hydrogen carbonate, dried, and evaporated. The product was

isolated by flash chromatography [ether-petroleum (1:9)]. The following were prepared in this way.

(a) 7,15,16,17-Tetrahydro-6H-cyclopenta[a]phenanthrene (**11a**). The alcohol (**8a**) (150 mg, 0.62 mmol) in toluene (40 ml) for 2 h gave the phenanthrene (**11a**) (110 mg, 80%), b.p. 220 °C at 0.1 mmHg (Found: C, 92.45; H, 7.0. C₁₇H₁₆ requires C, 92.7; H, 7.3%); δ (220 MHz) 2.20 (2 H, br), 2.65 (4 H, t), 3.00 (4 H, t), 7.10–7.40 (5 H, m), and 7.65 (1 H, d); m/z 220.124 (M^+ , C₁₇H₁₆ requires 220.125) and 191.

(b) 1,2,3,4,5,6-Hexahydrochrysene (**11b**). The alcohol (**8b**) (75 mg, 0.29 mmol) in toluene (40 ml) for 1 h gave the chrysene (**11b**) (48 mg, 70%), m.p. 108–109 °C (from petroleum) (lit.,¹¹ 112.5–113.5 °C); δ (220 MHz) 1.85–2.00 (4 H, m), 2.65–2.75 (4 H, m), 2.96–3.10 (4 H, m), 7.05–7.35 (5 H, m), and 7.85 (1 H, d).

(c) 1-Phenyl-9,10-dihydrophenanthrene (**11c**). The alcohol (**8c**) (90 mg, 3.2 mmol) in toluene (70 ml) for 12 h gave the phenanthrene (**11c**) (62 mg, 74%) as a yellow oil (Found: C, 93.5; H, 6.35. C₂₀H₁₆ requires C, 93.7; H, 6.3%); δ (220 MHz) 2.70 (2 H, t), 3.03 (3 H, t), 7.15 (3 H, m), 7.30 (3 H, m), 7.50 (2 H, d), 7.65 (2 H, d), and 7.85 (2 H, d).

(d) 1,2,3,4,7,8-Hexahydrobenzo[c]phenanthrene (**14**). The alcohol (**9**) (0.1 g, 0.39 mmol) in toluene (60 ml) gave the phenanthrene (**14**) (68 mg, 73%), b.p. 155 °C at 0.1 mmHg. This solidified on cooling, m.p. 77–78 °C (lit.,¹² 78 °C); δ (220 MHz) 1.55–1.75 (4 H, m), 2.40–2.60 (4 H, m), 2.80–2.90 (4 H, m), 7.05–7.35 (5 H, m), and 7.65 (1 H, d); m/z 234 (M^+), 192, and 179.

1,2,3,4,4a,5,7,8-Octahydrobenzo[c]phenanthrene (19 mg, 20%) was also isolated as an oil, b.p. 160 °C at 0.1 mmHg (Found: C, 91.6; H, 8.55. C₁₈H₂₀ requires C, 91.5; H, 8.5%); δ (220 MHz)

1.60–1.80 (7 H, m), 2.25 (4 H, t), 2.40 (2 H, t), 2.95 (2 H, t), 5.95 (1 H, t), 7.05 (1 H), and 7.10 (3 H); m/z 236.151 (M^+ ; C₁₈H₂₀ requires 236.156), 221, 207, 193, and 179.

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