o-Quinonoid Compounds. Part 19.[1] Relative Migratory Aptitudes for Doubly and Triply Bonded Groups in 1,3-Dimethyldibenz[e,g]indenes

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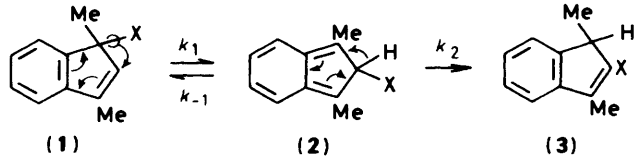
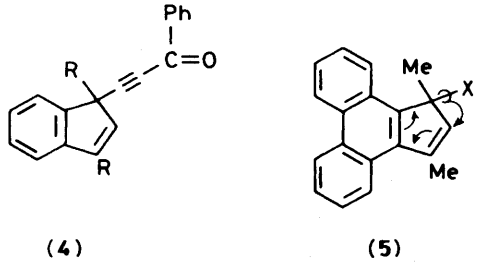
The 1,5-sigmatropic shift of unsaturated groups [CHO, CO_2Me, C≡N, (*E*)-CH=$CHCO_2Et$, (*E*)-CH=CHCOPh, C≡CCOPh] is *ca.* 10^2-times faster in the 1,3-dimethyldibenz[*e,g*]indenes (cyclopenta[*l*]phenanthrenes) (**5**; X = unsaturated group) than in the simple indenes (**1**). This permits observation of relatively clean rearrangement of triply-bonded migrating groups to give the 2-substituted dibenzindenes (**16**). The C≡N group migrates *ca.* 10^6-times more slowly than the CHO group, and the C≡CCOPh group migrates at least 500-times more slowly than the (*E*)-CH=CHCOPh group. The slow migration of triply bonded groups compared with doubly bonded groups in cyclopentadiene systems may be associated with increased strain in bridged rearrangement transition states.

Our study[2] of the migratory aptitudes of unsaturated groups in the 1,5-sigmatropic shift employed optically active indenes (**1**; X = migrating group) which upon 1,5-shift of X gave the symmetric 2*H*-indenes (**2**) (Scheme 1). For groups migrating more slowly than hydrogen $k_2 > k_{-1}$ in Scheme 1, and migratory aptitudes obtained from the rate of optical activity loss or



Scheme 1.

the rate of formation of 2-X-substituted indenes are equal.[2b] Our results for the migration of triply-bonded groups (C≡N, C≡CH) indicated that migration of these groups was very slow. Only small optical activity loss occurred after prolonged heating at 245 °C, and the expected 2-substituted indenes (**3**) could not be isolated. We undertook the present study to place the occurrence of 1,5-shift of these groups on a sound basis, to enquire into the reason(s) for the slow migration of triply-bonded groups about cyclopentadienes, and to provide a system suitable for the observation of the 1,5-sigmatropy of other slow migrators.

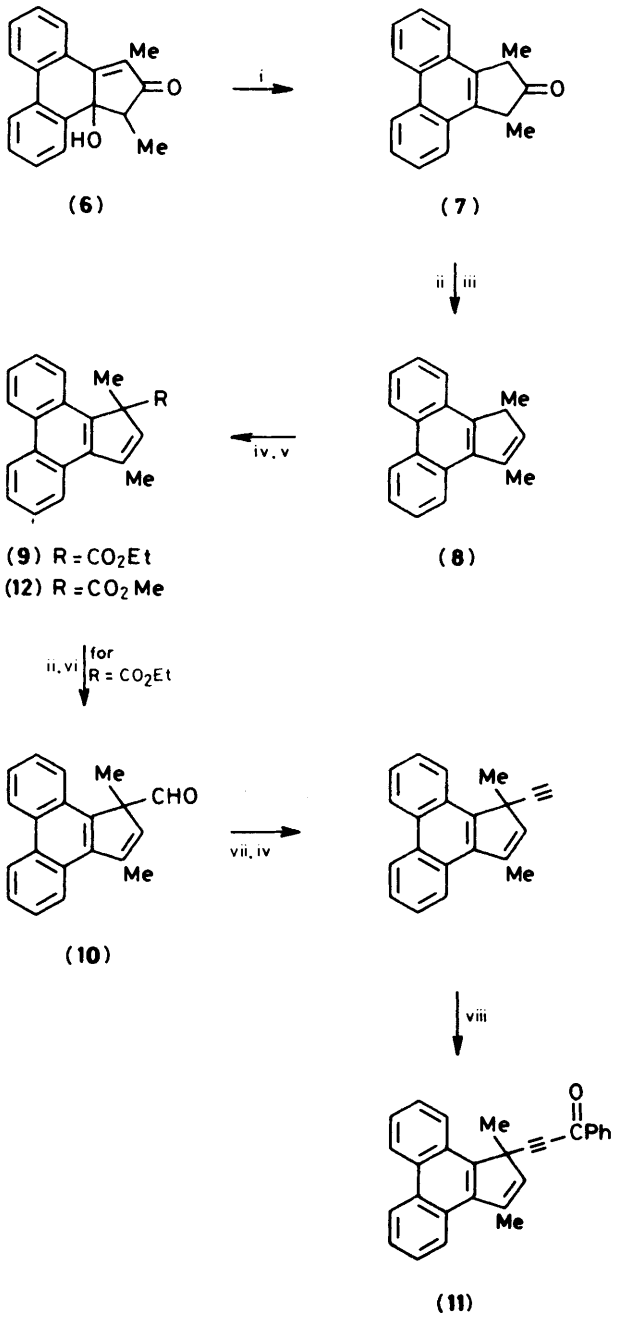


Since replacement of methyl groups in indenes (**1**) by phenyl groups is known to accelerate rearrangement,[2a] and since the *E*-benzoyl group accelerates vinyl migration by a factor of *ca.* 220,[2c] we first prepared compounds (**4**; R = Ph) and (**4**; R = Me). Rearrangement of these compounds required prolonged heating at high temperature (>235 °C). In both cases random decomposition of starting material and/or product prevented observation of clean rearrangement.

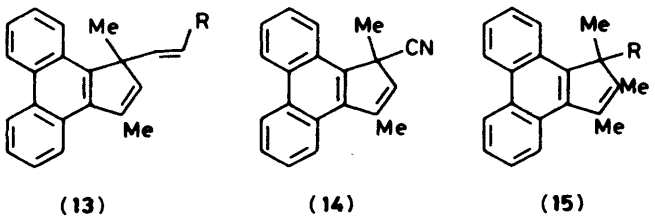
Since a 1,5-shift in fused indenes (**5**) would result in a smaller aromaticity loss than for compounds (**1**) we devoted some effort to the synthesis of such dibenzindenes (Scheme 2). The hydroxy ketone (**6**), readily available by base-catalysed condensation of phenanthroquinone with diethyl ketone,[3] was reduced (Zn/HOAc) to give the ketone (**7**) as a mixture of stereoisomers. Without separation this mixture was reduced ($LiAlH_4$) and the resulting stereoisomeric alcohols were dehydrated ($POCl_3$–pyridine) to give the indene (**8**). The lithium salt of compound (**8**) was converted into the ethyl ester (**9**) ($ClCO_2Et$), which was subsequently converted into the aldehyde (**10**) and then into the benzoylethynyl-substituted dibenzindene (**11**) (Scheme 2). The methyl ester (**12**) was prepared by reaction of the lithium salt of compound (**8**) with carbon dioxide and methylation (CH_2N_2) of the acid formed. Wadsworth–Emmons reaction of aldehyde (**10**) with the sodium salt of ethyl (diethoxy phosphoryl)acetate gave the (*E*)-ethoxycarbonyl-substituted indene (**13**; R = CO_2Et), and related reaction of aldehyde (**10**) with the sodium salt of diethyl (2-oxo-2-phenylethyl) phosphonoacetate gave enone (**13**; R = COPh). The aldehyde (**10**) was converted into the nitrile (**14**) *via* oxime formation followed by dehydration with acetic anhydride. The trimethyl-substituted indene (**15**; R = H) was readily available by dehydration ($POCl_3$–pyridine) of the alcohols obtained by reaction of the stereoisomeric ketones (**7**) with methyllithium. Carboxylation of the lithium salt (**15**; R = Li) gave the acid (**15**; R = CO_2H); after esterification (CH_2N_2), reduction with lithium aluminium hydride gave the alcohol (**15**; R = CH_2OH). This gave aldehyde (**15**; R = CHO) upon either Pfitzner–Moffat or Swern oxidation.

Rearrangement of Dibenz[e,g]*indenes* (*Cyclopenta*[l]*phenanthrenes*).—Thermal rearrangement of the dibenz[*e,g*]indenes followed the course of Scheme 3 to provide isolable 2-substituted products (**16**) in all cases. As expected, rearrangement was faster (*ca.* 100 times) than for the simple indenes (**1**) and the lower rearrangement temperature provided much cleaner reactions. The aromaticity of the central ring in phenanthrene, whilst small enough to allow lower temperature rearrangement to (**17**), was not so small as to allow formation of a mixture of products by subsequent indiscriminate hydrogen shifts in compounds (**16**).

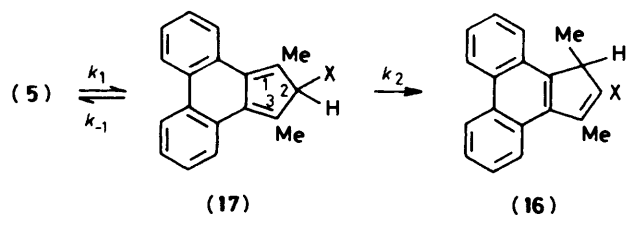
Unlike the simple aldehyde (**1**; X = CHO),[2a] the aldehyde (**15**; R = CHO) provided a temperature-dependent ^1H n.m.r. spectrum above 100 °C; the methyl resonances at δ_H 1.61 and 2.60 (C-1 and C-3 methyl groups respectively) broadened considerably up to 150 °C (the highest temperature employed).



Scheme 2. *Reagents and conditions:* i, Zn, HOAc; ii, $LiAlH_4$; iii, $POCl_3$, pyridine; iv, Bu^nLi, Et_2O; v, $ClCO_2Et$; vi, Me_2SO, $(COCl)_2$, CH_2Cl_2, −60 °C, then Et_3N; vii, PPh_3, CBr_4; viii, PhCOCl, Et_3N, $PdCl_2$·2Ph_3P (cat.), CuI (cat.).



At the same time the C-2 methyl resonance remained sharp. Line-shape analysis* of spectra taken at 10 °C intervals over this temperature range provided rate constants and activation



Scheme 3.

parameters (see Experimental section) showing that 1,5-formyl migration is some 550-times faster in (**15**; R = CHO) than in (**1**; X = CHO), and 400-times faster in (**15**; R = CHO) than in 1-formyl-1,2,3-trimethylindene. Rearrangement of compound (**5**; X = CO_2Me) to (**16**; X = CO_2Me) proceeded *ca.* 140-times more rapidly (k 6.23 × 10^{-5} s^{-1} at 190 °C) than the corresponding rearrangement of (**1**; X = CO_2Me). Importantly, rearrangement of the nitrile (**5**; X = CN) provided compound (**16**; X = CN) in a fairly clean reaction proceeding at 250 °C (k 19.0 × 10^{-5} s^{-1} in Ph_2O; k 22.3 × 10^{-5} s^{-1} at 254 °C in C_6D_6), *i.e.* the nitrile group migrates *ca.* 10^8-times more slowly than the formyl group. The acetylene (**5**; X = C≡CCOPh) also rearranged cleanly to the 2-isomer (**16**; X = C≡CCOPh) (k 3.06 × 10^{-5} s^{-1}; Ph_2O; 179 °C). Rearrangement of the olefin [**5**; X = (*E*)-CH=CHCOPh] proceeded under mild conditions (k 15.05 × 10^{-5} s^{-1}; Ph_2O; 104.5 °C). Thus migration of the olefinic group (*E*)-CH=CHCOPh is *ca.* 500-times faster than that of its acetylenic counterpart (C≡CCOPh). This rate difference probably underestimates the difference in migratory aptitude of the two groups.

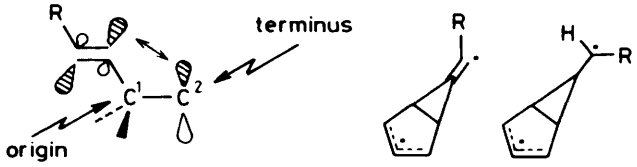
In the indenes (**1**) the (*E*)-CH=CHCOPh group migrates *ca.* 40-times faster than hydrogen,[2b,c] *i.e.* the (*E*)-CH=CHCOPh group is not a *slow* migrator. Accordingly, in the 2*H*-indene intermediate [**17**; X = (*E*)-CH=CHCOPh] derived by initial 1,5-shift, migration of the (*E*)-CH=CHCOPh group back to C-1 may strongly compete with corresponding H-shift leading to [**16**; X = (*E*)-CH=CHCOPh] and the rate of formation of the latter will underestimate the migratory aptitude of the (*E*)-CH=CHCOPh group. The relative migratory aptitude of hydrogen and the (*E*)-CH=CHCOPh group when in direct competition for the 1,5-shift as in intermediate [**17**; X = (*E*)-CH=CHCOPh] is not known. The rate constants of Scheme 3 and the rate of formation of compounds (**16**) ($k_{obs.}$) are related by equation (1). Thus if k_{-1}/k_2 = **40** [the relative migratory

$$k_{-1}/k_2 = (k_1/k_{obs.}) - 1 \qquad (1)$$

aptitude of CH=CHCOPh and H in the indenes (**1**)] $k_{obs.}$ could underestimate the migratory aptitude of the (*E*)-CH=CHCOPh group by a factor of *ca.* **40**. In the indenes (**1**) racemisation rate constants show the (*E*)-CH=CHCOPh group to migrate *ca.* 1 600-times faster than the CO_2Me group, an undoubtedly slow migrator.[2b] The difference in the rate of rearrangement of compounds [**5**; X = (*E*)-CH=CHCOPh] and (**5**; X = CO_2Me) is *ca.* 10^3, suggesting that reversibility in the initial 1,5-shift produces a $k_{obs.}$ some two-thirds of the real migratory aptitude of the (*E*)-CH=CHCOPh group. Reversibility should be less important for the (*E*)-CH=CHCO$_2$Et group which migrates only 3-times faster than hydrogen in the indenes (**1**);[2b,c] [**5**; X = (*E*)-CH=CHCO$_2$Et] rearranges to [**16**; X = (*E*)-CH=CHCO$_2$Et] at 117 °C at a rate given by k 7.44 × 10^{-5} s^{-1}; Ph_2O, *i.e.* 6-times more slowly than rearrangement of [**5**; X = (*E*)-CH=CHCOPh]. The corresponding rate difference for the racemisation of indenes (**1**) is *ca.* 8.[2c] This small difference in rate ratio

* Analysis kindly performed by Dr. R. J. Bushby.

suggests that the rate of formation of compounds [**16**; X = (*E*)-CH=CHCOPh] underestimates the migratory aptitude of the migrating group by no more than a factor of 2. The CH=CHCOPh group may accelerate hydrogen rearrangement to [**16**; X = (*E*)-CH=CHCOPh] either by speeding 1,5-sigmatropic shift of hydrogen or by permitting formation of an intermediate enol.



(**18**) (**19**) (**20**)

The slow migration of triply-bonded groups observed here is at first sight consistent with our view that migratory aptitude parallels π^* energy of the migrating groups. Calculated π^* energies for ground-state acetylenes are higher than those of the corresponding olefins.[4] However, electron-deficient alkynes tend to be more reactive than the corresponding olefins in cycloaddition reactions, and this has been explained by a low-energy bending of the acetylene in the pericyclic transition state. Such bending has been calculated[4] to reduce the π^* energy of an alkyne below that of a corresponding alkene. If such a bent acetylene is represented as in structure (**18**) the difficulty in effecting good overlap between the π^*-orbital of the acetylene and an occupied orbital at the migration terminus is clear. This difficulty stems from the fact that 1,5-shift in cyclopentadiene is also a 1,2-shift. If bonding as indicated in structure (**18**) were to be secured, the transition state would have methylenecyclopropane character (**19**) rather than the cyclopropane character (**20**) which would attend migration of a double-bonded group. Since methylenecyclopropane is 14 kcal mol^{-1}* more strained than cyclopropane[5] the slow rearrangement of triply-bonded groups could be understood. It should be noted that the ring-formation leading to transition state contributor (**19**) corresponds to a forbidden 3-*exo-dig* process, whilst the ring formation implied by the transition state contributor (**20**) is an allowed 3-*exo-trig* process.[6] The relatively slow migration of triply-bonded groups in cyclopentadienes is consistent either with secondary interaction between the π^*-orbital of the migrating group and the migration terminus,[2b,c] or what may be equivalent, important formation of the new bond to the migration terminus prior to cleavage of the old bond.[7] Substituent effects at the migration origin and terminus may help define the degree of cleavage of the old bond at the rearrangement transition state.

The large geometrical constraint on the 1,5-shift of triply-bonded groups described here will only apply when the 1,5-shift is also a 1,2-shift, *i.e.* for rearrangement over a cyclopentadiene. In the following paper migratory aptitudes are determined for doubly- and triply-bonded groups over a cycloheptatriene system in which the migration origin and terminus are further separated.

Experimental

M.p.s. were determined with a Kofler hot-stage apparatus and are uncorrected. Unless otherwise stated, i.r. spectra refer to Nujol mulls, u.v. spectra to ethanol solutions, and ^{1}H n.m.r. spectra to solutions in deuteriochloroform measured with a Perkin-Elmer R12 (60 MHz) or R32 (90 MHz) spectrometer. Low-resolution mass spectra were obtained with a Kratos MS25 instrument and accurate mass measurements were made using a Kratos MS9150 instrument. Where accurate mass measurement was used to establish molecular formulae the purity of the sample was checked by t.l.c. in more than one solvent system as well as by n.m.r. measurements, and for crystalline material by crystallisation to constant m.p. Chromatography on silica refers to short-column chromatography[8] over Kieselgel G (Merck). Ether refers to diethyl ether (except in the description of the thermolyses) and light petroleum to the fraction b.p. 60—80 °C. Thermolyses were carried out in base-washed sealed tubes (2 mm i.d.). Prior to thermolysis, solutions were degassed using five freeze–pump–thaw cycles. The progress of thermolyses was followed using ^{1}H n.m.r. spectroscopy (90 MHz).

1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*. (**8**).—1,11b-Dihydro-11b-hydroxy-1,3-dimethylcyclopenta[l]phenanthren-2-one (**6**) (33 g), zinc dust (40 g), and glacial acetic acid (600 ml) were stirred together and boiled under reflux (10 min). More zinc dust (40 g) was added and the mixture was boiled under reflux for a further 10 min, then more zinc dust (80 g) was added and the mixture was refluxed for another 20 min; finally another quantity of zinc dust (80 g) was added and the mixture was again refluxed for 20 min. The cooled product was filtered and the inorganic residue was washed with dichloromethane until the washings were colourless. The combined filtrate and washings were evaporated under reduced pressure to give a residue which was taken up in dichloromethane; the organic extract was washed successively with saturated aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to give 1,3-dihydro-1,3-dimethylcyclopenta[*f*]phenanthren-2-one (**7**) as a mixture of *cis* and *trans* isomers (19.25 g, 62%), m.p. 86—95 °C; $\nu_{max.}$ 1 745, 1 611, and 1 238 cm^{-1}; δ_H(60 MHz) 1.62 (6 H, d, *J* 7 Hz), 4.02 (2 H, q, *J* 7 Hz), and 7.5—9.0 (8 H, m).

This crude product (11.15 g) in 1,2-dimethoxyethane (DME) (240 ml) was stirred under nitrogen at *ca.* 20 °C and lithium aluminium hydride (4 g) was added in portions during 10 min. After the mixture had been stirred at 20 °C for 1 h water was added (**CARE!**) and the product was isolated in ether. The product obtained on work-up (11.1 g, 99%) had m.p. 108—118 °C; $\nu_{max.}$ 3 350 and 1 340 cm^{-1}; δ_H(60 MHz) 1.27—1.62 (6 H, 2 br, d, *J* 7 Hz), 2.37 (1 H, br s, exch. D_2O), 3.5—4.5 (2 H, br, q, *J* 7 Hz), and 7.5—9.0 (8 H, m).

To a stirred mixture of these isomers of 2,3-dihydro-1,3-dimethyl-1*H*-cyclopenta[*f*]phenanthren-2-ol (99 g) in pyridine (10 ml) was added dropwise phosphoryl trichloride (8.1 g), and the mixture was heated to 125—130 °C and stirred under nitrogen for 24 h. The cooled product was poured onto ice-water, the mixture was acidified with 1M-sulphuric acid, and the product was extracted into dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to give a crude product (8.2 g) which was purified by chromatography on silica (500 g) with light petroleum–benzene (3:1) as eluant to give 1,3-*dimethyl*-1H-*cyclopenta*[*f*]*phenanthrene*, (**8**), (4.7 g, 56%) as a white solid, m.p. 113—114.5 °C (from benzene–light petroleum) (Found: C, 93.4; H, 6.6. $C_{19}H_{16}$ requires C, 93.4; H, 6.6%); $\lambda_{max.}$ 333, 323, 260.5, and 243 nm (ε 7 800, 8 500, 20 500, and 18 300 l mol^{-1} cm^{-1}); δ_H(90 MHz) 1.42 (3 H, d, *J* 7 Hz), 2.65 (3 H, t, *J* 1.5 Hz), 3.77 (1 H, dm, *J* 7 and 1.5 Hz), 6.34 (1 H, m, *J* 1.5 Hz), and 7.3—8.85 (8 H, m); *m/z* 244, 229, 227, 215, 202, 122, 113, 101, 69, and 44 (100, 160, 74, 6, 9, 6, 22, 14, 7, and 7%).

1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylic Acid* (**5**; X = CO_2H).—To a vigorously stirred solution of the foregoing indene (**8**) (4.6 g) in ether (150 ml) at 20 °C under nitrogen was added Bu^{n}Li in hexane (20 ml; 67 mg ml^{-1} Bu^{n}Li). After the mixture had been stirred for a further 30 min the product was poured into a slurry of ground solid carbon di-

* 1 kcal = 4.184 kJ.

oxide in ether and the mixture was allowed to come to room temperature (2.5 h). Extraction of the product into 2M-NaOH (3 × 700 ml), acidification of the basic extract with conc. HCl at 0—5 °C, and isolation in dichloromethane gave, after work-up, crude 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylic acid* (**5**; X = CO_2H) (4.5 g), m.p. 189—190 °C (decomp.) (from benzene–light petroleum) (Found: C, 83.55; H, 5.45. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.6%).

Methyl 1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (**12**).—A solution of 1,3-dimethyl-1*H*-cyclopenta-[*f*]phenanthrene (**8**) (120 mg) in ether (4 ml) was treated at 20 °C with n-butyl-lithium in hexane (0.5 ml; 80 mg Bu^nLi ml^{-1}) while being stirred under nitrogen. After being stirred for another 30 min the mixture was treated with a solution of methyl chloroformate (100 mg) in ether (1 ml) the mixture was stirred for another 15 min. Addition of water, extraction into ether, and chromatography of the product on silica in benzene gave recovered starting material (**8**) (45 mg). Continued elution of the column gave the *title ester* (**12**) (80 mg), m.p. 158—160 °C (from chloroform–ethanol) (Found: C, 83.3; H, 6.25%; M^+, 302.13. $C_{21}H_{18}O_2$ requires C, 83.4; H, 6.0%; *M*, 302.1307); $\nu_{max.}$ 1 730 and 1 235 cm^{-1}; δ_H (60 MHz) 1.7 (3 H, s), 2.65 (3 H, d, *J* 1.5 Hz), 3.45 (3 H, s), 6.25 (1 H, q, *J* 1.5 Hz), 7.3—7.9 (5 H, m), and 8.4—8.85 (3 H, m).

Ethyl-1,3-*Dimethyl* 1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (**9**).—A solution of 1,3-dimethyl-1*H*-cyclopenta[*f*]phenanthrene (**8**) (5 g, 20.5 mmol) in ether (150 ml) was stirred at 0—5 °C under nitrogen during the addition of n-butyl-lithium (14.8 ml of 1.55M-Bu^nLi in hexane; 22.9 mmol). After the mixture had been stirred at 20 °C for 30 min, ethyl chloroformate (4.25 ml) was added and the mixture was stirred for another 15 min. The product was washed with water and the ether solution was dried ($MgSO_4$) and evaporated to give a residue (7 g) which was chromatographed on silica in benzene–light petroleum (4:1) as eluant to give *ethyl* 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (**9**) (4.6 g, 72%), m.p. 89—91 °C (from ethanol) (Found: C, 83.55; H, 6.45%; M^+, 316.1462. $C_{22}H_{20}O_2$ requires C, 83.5; H, 6.3%; *M*, 316.1463); $\nu_{max.}$ 1 725 cm^{-1}; $\lambda_{max.}$ 335sh, 323, 272sh, 263, and 241 nm (ε 12 000, 13 300, 32 900, 41 400, and 50 900); δ_H(90 MHz) 1.01 (3 H, t, *J* 7 Hz), 1.75 (3 H, s), 2.75 (3 H, d, *J* 1.5 Hz), 4.07 (2 H, q, *J* 7 Hz), 6.37 (1 H, q, *J* 1.5 Hz), and 7.5—8.9 (8 H, m); *m/z* 316, 243, 228, 202, 113, 83, 69, and 44 (97.7, 100, 74.8, 13.1, 3.6, 4.9, 3.9, and 14.9%).

(1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*yl*)*methanol* (**5**; X = CH_2OH).—A solution of the foregoing ethyl ester (7.9 g) in ether (200 ml) was stirred at −20 °C under nitrogen, and lithium aluminium hydride (7.9 g) was added in small portions during 5 min. The product was stirred at −20 °C (1 h) and then allowed to come to 20 °C. Excess of lithium aluminium hydride was destroyed by careful addition of water. The product was acidified with dil. hydrochloric acid (2M), and extracted into ether, and the extracts were washed with water, dried ($MgSO_4$), and evaporated to give a residue (6.7 g) which was chromatographed on silica (500 g) in benzene as eluant to give (1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*methanol* (**5**; X = CH_2OH) (6.6 g, 96%), m.p. 144—145 °C (from benzene–light petroleum) (Found: C, 87.65; H, 6.65%; M^+, 274.1364. $C_{20}H_{18}O$ requires C, 87.6; H, 6.6%; *M*, 274.1358); $\nu_{max.}$ 3 500—3 200 and 1 380 cm^{-1}; $\lambda_{max.}$ 334, 322, 262, and 242 nm (ε 9 100, 10 300, 35 100, and 34 500); δ_H(90 MHz) 1.50 (1 H, br, OH, exch. D_2O), 1.50 (3 H, s), 2.63 (3 H, d, *J* 1.5 Hz), 3.83 (1 H, d, *J* 10 Hz), 4.10 (1 H, d, *J* 10 Hz), 6.31 (1 H, q, *J* 1.5 Hz), and 7.4—9.0 (8 H, m).

1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbaldehyde* (**10**).—A solution of dimethyl sulphoxide (3.6 ml, 46.6 mmol) in dichloromethane (15 ml) was added dropwise to a solution of oxalyl chloride (2.1 ml, 23.3 mmol) in dichloromethane (75 ml) at −50 to −60 °C under nitrogen. After this mixture had been stirred for 2 min, a solution of the foregoing alcohol (**5**; X = CH_2OH) (5.8 g, 21.2 mmol) in dichloromethane (30 ml) and dimethyl sulphoxide (10 ml) was added during 5 min and the mixture was stirred (15 min) at −50 to −60 °C. Triethylamine (14.8 ml, 106 mmol) was added and the mixture was stirred for a further 5 min. Dil. hydrochloric acid (2M) was added and the product was extracted into ether; the extract was washed successively with aqueous sodium hydroxide (2M), dil. (2M) hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated. The crude product (5.65 g) was chromatographed on silica (500 g) in benzene–ether (9:1) as eluant to give 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbaldehyde* (**10**) (5.45 g, 95%), m.p. 106—107 °C (from benzene–light petroleum) (Found: C, 87.75; H, 6.0%; M^+, 272.1201. $C_{20}H_{16}O$ requires C, 88.2; H, 5.9%; *M*, 272.1201); $\nu_{max.}$ 1 723 and 1 708 cm^{-1}; $\lambda_{max.}$ 323, 281sh, 266, 254, and 245 nm (ε 7 100, 17 400, 23 700, 21 800, 24 600); δ_H(90 MHz) 1.71 (3 H, s), 2.78 (3 H, d, *J* 1.5 Hz), 6.07 (1 H, q, *J* 1.5 Hz), 7.5—8.9 (8 H, m), and 8.45 (1 H, s, CHO).

The aldehyde readily isomerises to 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-2-*carbaldehyde*. Isolation of compound (**10**) should therefore be attempted at or below 20 °C. Even gentle heating in the presence of traces of acidic or basic impurities leads to the 2-carbaldehyde isomer. The 2-*isomer* was purified by chromatography on silica in ether–benzene (1:9) as eluant, followed by crystallisation from ethanol, m.p. 204—206 °C (Found: C, 88.25; H, 6.0%; M^+, 272.1197); $\nu_{max.}$ 1 641 cm^{-1}; $\lambda_{max.}$ 360.5, 299.5sh, and 264 nm (ε 12 900, 10 500 and 22 300); δ_H(90 mHz) 1.56 (3 H, d, *J* 7 Hz), 3.02 (3 H, d, *J* 1.5 Hz), 4.20 (1 H, qq, *J* 7 and 1.5 Hz), 7.5—8.9 (8 H, m), and 10.29 (1 H, s, CHO).

1-(2,2-*Dibromovinyl*)-1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene* (**5**); X = CH=CBr_2).—Triphenylphosphine (46.2 g, 0.176 mol) was added to a solution of carbon tetrabromide (34.9 g, 0.105 mol) in dichloromethane (100 ml) at 20 °C under nitrogen, and the mixture was stirred at 20 °C (15 min). A solution of the aldehyde (**10**) (5.45 g, 0.02 mol) in dichloromethane (30 ml) was added quickly and the mixture was stirred at 20 °C for a further 90 min. The product was poured into light petroleum and cooled to 0 °C (maintained 1 h). The product was filtered and the filtrate was evaporated to give a residue (7.9 g) which was chromatographed on silica (500 g) in light petroleum as eluant to give 1-(2,2-*dibromovinyl*)-1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene* (**5**; X = CH=CBr_2) (3.0 g, 31%), m.p. 104—107 °C (from light petroleum) (Found: C, 59.0; H, 3.7; Br, 37.55%; M^+, 429.9580. $C_{21}H_{16}Br_2$ requires C, 58.9; H, 3.7; Br, 37.4%. $C_{21}H_{16}{}^{81}Br_2$ requires *M*, 429.9580); $\nu_{max.}$ 3 065, 805, and 613 cm^{-1}; $\lambda_{max.}$ 273, 262, 241, and 227 nm (ε 13 300, 16 200, 21 900, and 30 000); δ_H(90 MHz) 1.60 (3 H, s), 2.64 (3 H, d, *J* 1.5 Hz), 6.37 (1 H, q, *J* 1.5 Hz), 6.95 (1 H, s, olefinic), and 7.5—8.9 (8 H, m).

1-*Ethynyl*-1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene* (**5**; X = C≡CH).—A solution of the foregoing dibromide (2.3 g, 5.35 mmol) in ether (100 ml) was stirred at −70 °C under nitrogen during the addition of n-butyl-lithium in hexane (11.5 ml of 1.5M-solution; 17.25 mmol). After being stirred at −70 °C for a further 30 min, the mixture was warmed to −30 °C and stirred for 1 h. The product was quenched with water, and the ether layer was washed successively with saturated aqueous ammonium chloride and water, and dried ($MgSO_4$), and the residue obtained on evaporation of the solvent was chromatographed on silica (200 g) in dichloromethane–light

petroleum (1:4) as eluant to give 1-*ethynyl*-1,3-*dimethyl*-1H-*cyclopenta*[*l*]*phenanthrene* (**5**; X = C≡CH) (1.13 g, 83%), m.p. 124—126 °C (from light petroleum) (Found: C, 93.8; H, 5.85%; M^+, 268.1250. $C_{21}H_{16}$ requires C, 94.0; H, 6.0%; *M*, 268.1252); $\nu_{max.}$ 3 300 and 2 110 cm^{-1}; $\lambda_{max.}$ 334, 323, 278sh, 271sh, 263, and 239 nm (ε 9 000, 9 800, 17 000, 24 100, 29 000, and 34 400); δ_H(90 MHz) 1.73 (3 H, s), 2.30 (1 H, s, acetylenic), 2.65 (3 H, d, *J* 1.5 Hz), 6.40 (1 H, q, *J* 1.5 Hz), and 7.4—8.85 (8 H, m).

(1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*ethynyl Phenyl Ketone* (**11**).—Dichlorobis(triphenylphosphine)palladium(II) (0.4 mg, 0.4 mmol) and copper(I) iodide (0.4 mg) were added to a well stirred solution of 1-ethynyl-1,3-dimethyl-1*H*-cyclopenta[*l*]phenanthrene (100 mg, 0.4 mmol) and benzoyl chloride (56 mg, 0.4 mmol) in triethylamine (40 ml) at 20 °C under nitrogen, and the mixture was stirred at 20 °C for 15 h. Methanol was added to the mixture, the solvent was removed under reduced pressure, the residue was dissolved in benzene, and the solution was washed successively with dil. hydrochloric acid (2M) and water, dried ($MgSO_4$), and evaporated to give a residue (150 mg) which was chromatographed on silica (20 g) in dichloromethane–light petroleum (1:1) as eluant to give the *title ketone* (**11**) (100 mg), m.p. 106—107 °C (from light petroleum) (Found: C, 90.0; H, 5.7%; M^+, 372.1504. $C_{28}H_{20}O$ requires C, 90.3; H, 5.4%; *M*, 372.1514); $\nu_{max.}$ 2 200 and 1 640 cm^{-1}; $\lambda_{max.}$ 322, 263, and 240 nm (ε 7 800, 36 500, and 37 200); δ_H(90 MHz) 1.88 (3 H, s), 2.75 (3 H, d, *J* 1.5 Hz), 6.48 (1 H, q, *J* 1.5 Hz), and 7.3—8.9 (13 H, m).

Ethyl 3-(1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*propenoate* (**13**; R = CO_2Et).—A solution of triethyl phosphonoacetate [ethyl (diethoxyphosphoryl)acetate] (225 mg, 1 mmol) in DME (1 ml) was added quickly to a suspension of 50% sodium hydride (50 mg; 1 mmol) in DME (1.5 ml) under nitrogen at 0—5 °C. The mixture was stirred at 20 °C (1 h); a solution of the aldehyde (**10**) (225 mg, 0.825 mmol) in DME (1 ml) was then added, and the mixture was stirred at 20 °C for a further 30 min. The product was diluted with water, and extracted into ether, the extract was washed with water, dried ($MgSO_4$), and evaporated, and the residue (380 mg) was chromatographed on silica (50 g) in benzene as eluant to give (*E*)-{ethyl 3-(1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*propenoate*} (**13**; R = CO_2Et) (60 mg, 21%), m.p. 121—123 °C (from benzene–light petroleum) (Found: C, 83.95; H, 6.6%; M^+, 342.1618. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.4%; *M*, 342.1620); $\nu_{max.}$ 1 715 and 1 645 cm^{-1}; $\lambda_{max.}$ 322, 282sh, 271, 262.5, and 241 nm (ε 9 100, 19 800, 23 900, 30 400, and 34 200); δ_H(90 MHz) 1.23 (3 H, t, *J* 8 Hz), 1.67 (3 H, s), 2.70 (3 H, d, *J* 1.5 Hz), 4.15 (2 H, q, *J* 8 Hz), 6.05 (1 H, d, *J* 16 Hz), 6.15 (1 H, q, *J* 1.5 Hz), 6.85 (1 H, d, *J* 16 Hz), and 7.5—8.9 (8 H, m).

(E)-2-(1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*vinyl Phenyl Ketone* (**13**; R = COPh).—A solution of diethyl phosphonoacetophenone [diethyl (2-oxo-2-phenylethyl)phosphonate] (115 mg) in DME (1 ml) was added quickly to a suspension of 50% sodium hydride–mineral oil (24 mg) in DME (1 ml) under nitrogen at 0—5 °C. After the mixture had been stirred at 20 °C for 1 h, a solution of the aldehyde (**8**) (140 mg) in DME (0.5 ml) was added and the reaction mixture was stirred at 20 °C for a further 1 h. The product was diluted with water, and extracted into ether, and the extract was washed with water, dried ($MgSO_4$), and evaporated to give a residue which, after chromatography on silica (20 g) in benzene as eluant, gave (E)-2-(1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*vinyl phenyl ketone* (**13**; R = COPh) (26 mg, 13%), m.p. 147—148 °C (from ethanol) (Found: M^+, 374.1673. $C_{28}H_{22}O$ requires *M*, 374.1671); $\nu_{max.}$ 1 665, 1 655sh, 1 605, 1 585, and 1 580 cm^{-1}; $\lambda_{max.}$ 322, 262, and 245sh nm (ε 16 500, 67 300, and 59 800); δ_H(90 MHz) 1.75 (3 H, s), 2.70 (3 H, d, *J* 1.5 Hz), 6.25 (1 H, q, *J* 1.5 Hz), 7.00 (2 H, s, olefinic), 7.35—8.0 (10 H, m), and 8.5—8.9 (3 H, m). In the presence of $Pr(fod)_3$* the singlet for the olefinic protons at δ_H 7.0 appeared as an AB-system at δ_H 4.55 (1 H, d, *J* 13 Hz), and 4.87 (1 H, d, *J* 13 Hz); *m/z* 374, 359, 269, 252, 105, and 77 (100, 78.5, 24.1, 28.9, 99.1, and 64.3%).

The Oxime of 1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbaldehyde* (**10**).—Hydroxylamine hydrochloride (67.5 mg) was dissolved in a mixture of ethanol (2.7 ml) and water (0.3 ml), and a solution of sodium acetate (101 mg) dissolved in a mixture of ethanol (2.7 ml) and water (0.3 ml) was added, followed by a solution of the aldehyde (**10**) (90 mg) in dichloromethane (6 ml), while the mixture was being stirred under nitrogen. After being stirred for 1.5 h, the product was diluted with water and extracted into ether, and the extract was washed successively with dil. hydrochloric acid (2M) and water, dried ($MgSO_4$), and evaporated. Chromatography of the crude product on silica in dichloromethane as eluant gave the *title compound* (72 mg) (Found: M^+, 287.1300; $C_{20}H_{17}NO$ requires *M*, 287.1310); $\nu_{max.}$ 3 270 cm^{-1}; δ_H(60 MHz) 1.7 (3 H, s), 2.7 (3 H, d, *J* 1.5 Hz), 6.2 (1 H, m, olefinic), 7.15 (1 H, s), and 7.4—8.0 (8 H, m).

1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbonitrile* (**14**).—A solution of the foregoing oxime (72 mg) in acetic anhydride (10 ml) was boiled under reflux (45 min) under nitrogen. Acetic anhydride was removed by heating under reduced pressure, and the residue was chromatographed on silica (20 g) in benzene as eluant to give 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbonitrile* (**14**) (53 mg), m.p. 120—122 °C (from ethanol) (Found: M^+, 269.1205. $C_{20}H_{15}N$ requires *M*, 269.1204); $\nu_{max.}$ 2 242 cm^{-1}; δ_H(90 MHz) 1.82 (3 H, s), 2.66 (3 H, d, *J ca.* 1 Hz), 6.4 (1 H, q, *J ca.* 1 Hz), and 7.5—8.8 (8 H, m).

1,2,3-*Trimethyl*-1H-*cyclopenta*[l]*phenanthrene* (**15**; R = H).—The previously described mixture of *cis*- and *trans*-1,3-dihydro-1,3-dimethylcyclopenta[*l*]phenanthren-2-one (2.7 g) was suspended in ether (100 ml) and the mixture was added to a solution of methyl-lithium [from lithium shot (2.2 g) and methyl iodide (25 g)] in ether (150 ml), and the mixture was stirred under nitrogen at 20 °C (2 h). Water was added, the volume of ether was made up to 800 ml, and the organic layer was washed successively with dil. hydrochloric acid (1M) and water, dried ($MgSO_4$), and evaporated to give the fairly pure tertiary alcohol (2.5 g). Without further purification the alcohol (2.3 g), pyridine (6.3 g), and phosphoryl trichloride (4.1 g) were combined in dichloromethane (40 ml), and the mixture was boiled under reflux (15.5 h). The cooled product was diluted with water and extracted into dichloromethane. The extract was washed successively with water, dil. hydrochloric acid (2M), and water again, dried ($MgSO_4$), and evaporated. Crystallisation of the crude product from chloroform—methanol gave the *title compound* (**15**; R = H) (718 mg), m.p. 144—147 °C (Found: M^+, 258.1403. $C_{20}H_{18}$ requires *M*, 258.1408); $\nu_{max.}$ 763 and 730 cm^{-1}; δ_H(60 MHz) 1.37 (3 H, d, *J* 7 Hz), 2.05 (3 H, br s), 2.5 (3 H, br s), 3.48 (1 H, qm, *J* 7 Hz), and 7.3—8.9 (8 H, m).

1,2,3-*Trimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylic Acid* (**15**; R = CO_2H).—The foregoing indene (200 mg) was dissolved in ether (15 ml) and the solution was stirred and treated with n-butyl-lithium in hexane (1 ml of a solution containing 67 mg ml^{-1}) at 20 °C under nitrogen. After being stirred for a further 15 min, the product was poured into an ether–solid carbon dioxide slurry and the mixture was allowed

* Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione.

to warm to 20 °C (30 min). Extraction of the ethereal solution with dil. (2M) sodium hydroxide, acidification of the basic extracts with conc. hydrochloric acid at 0—5 °C, and extraction with ether gave the crude acid (150 mg). Recrystallisation from chloroform gave the *title compound* (**15**; R = CO_2H) (120 mg), m.p. 164—167 °C (Found: M^+, 302.1302. $C_{21}H_{18}O_2$ requires *M*, 302.1307); $\nu_{max.}$ 3 200—2 300 and 1 695 cm^{-1}; δ_H(90 MHz) 1.65 (3 H, s), 2.08 (3 H, br s), 2.63 (3 H, br s), and 7.5—8.9 (8 H, m); the CO_2H proton was not detected.

Reaction of the acid with diazomethane in ether in the usual way gave the corresponding *methyl ester* (Found: M^+, 316.1475. $C_{22}H_{20}O_2$ requires *M*, 316.1463); $\nu_{max.}$ 1 725 cm^{-1}; δ_H(60 MHz) 1.65 (3 H, s), 2.00 (3 H, br s), 2.58 (3 H, br s), 3.5 (3 H, s), and 7.3—9.0 (8 H, m).

(1,2,3-*Trimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*methanol* (**15**; R = CH_2OH).—A solution of the foregoing ester (23 mg) in ether (2 ml) was stirred at −20 °C under nitrogen. Lithium aluminium hydride (25 mg) was added and the mixture was stirred for a further 2 h at −20 °C. Addition of water at −20 °C and isolation in ether in the usual way gave the *title compound* (**15**; R = CH_2OH) (18 mg) (Found: M^+, 288.1508. $C_{21}H_{20}O$ requires M^+, 288.1514); δ_H(60 MHz) 1.2 (1 H, br s, exch. D_2O), 1.4 (3 H, s), 2.0 (3 H, br s), 2.58 (3 H, br s), 3.93 (1 H, d, *J* 12 Hz), 4.3 (1 H, d, *J* 12 Hz), and 7.4—8.9 (8 H, m).

1,2,3-*Trimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbaldehyde* (**15**; R = CHO).—A mixture of dimethyl sulphoxide (250 mg), benzene (250 mg), dicyclohexylcarbodi-imide (50 mg), pyridinium trifluoroacetate (7 mg), and (1,2,3-trimethyl-1*H*-cyclopenta[*l*]phenanthren-1-yl)methanol (20 mg) was stirred under nitrogen (20 h). The product was diluted with ether, and the solution was stirred with a few crystals of oxalic acid, cooled to −15 °C (for 20 min), and filtered. The filtrate was washed with water (4 ×), dried ($MgSO_4$), and evaporated to give a residue (15 mg) which was chromatographed on silica in benzene–light petroleum (85:15) as eluant to give the *title compound* (**15**; R = CHO) (7 mg), m.p. 118—119 °C (from benzene–light petroleum) (Found: C, 88.15; H, 6.45%. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%); $\nu_{max.}$ 1 710 cm^{-1}; δ_H(60 MHz) 1.61 (3 H, s), 1.91 (3 H, br s), 2.60 (3 H, br s), 7.60 (5 H, m, ArH), 8.4 (1 H, s, CHO), and 8.7 (3 H, m, ArH). Between 100 and 150 °C the methyl resonances at δ_H 1.61 and 2.60 (90 MHz) broadened markedly, whilst that at δ_H 1.91 did not change. Line-shape analysis of spectra taken at 10 °C intervals in this temperature range gave the following *k* values (s^{-1}): 3.2 (100), 5.4 (110), 8.5 (120), 17.2 (130), 30.0 (140), and 42.0 (150 °C); $\Delta G^{\ddagger}$ 16.0 ± 0.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ −13.9 ± 1.7 cal K^{-1} mol^{-1}, ΔG^{*} (250 °C) 20.1 ± 0.8 kcal mol^{-1}, E_a 16.8 ± 0.7 kcal mol^{-1}, log *A* 10.3 ± 0.4. Line shapes were generated using a locally modified version of a program written by Dr. B. Mann (Sheffield University) whose gift of the original version is gratefully acknowledged.[9]

Thermolysis of Methyl 1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carboxylate* (**12**).—The title compound (40 mg) was heated in diphenyl ether (0.4 ml) in a constant-temperature bath at 190 °C, with reaction progress monitored by n.m.r. spectroscopy (*k* 6.23 × 10^{-5} s^{-1}). After being heated for 27 h, the total product was chromatographed on silica (43 g) in benzene as eluant to give *methyl* 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-2-*carboxylate* (**16**; X = CO_2Me) (35 mg), m.p. 165—168 °C (from chloroform–ethanol) (Found: C, 83.1; H, 5.85%. $C_{21}H_{18}O_2$ requires C, 83.4; H, 6.0%); δ_H(60 MHz) 1.55 (3 H, d, *J* 7 Hz), 3.06 (3 H, d, *J* 1.5 Hz), 3.9 (3 H, s), 4.1 (1 H, qm, *J* 7 Hz), and 7.5—8.9 (8 H, m).

Thermolysis of 1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-1-*carbonitrile* (**14**).—The title compound (14 mg), diphenyl ether (0.4 g), and a trace of tetramethylsilane were deoxygenated (5 freeze–pump–thaw cycles), and the tube was sealed and heated in a constant-temperature bath at 250 °C. Reaction progress was followed by ^1H n.m.r. spectroscopy (*k* 1.90 × 10^{-4} s^{-1}). After being heated for 6 h, the product was transferred to a flask and most of the diphenyl ether was removed at 120 °C (0.02 mmHg). The residue (12 mg) was chromatographed on silica (20 g) in benzene to give 1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthrene*-2-*carbonitrile* (**16**; X = CN) (9.3 mg, 63%), m.p. 189—191 °C (from benzene–light petroleum) (Found: C, 89.25; H, 5.6; N, 5.1. $C_{20}H_{15}N$ requires C, 89.2; H, 5.6; N, 5.2%); δ_H(90 MHz) 1.57 (3 H, d, *J* 7 Hz), 2.85 (3 H, d, *J* 1.5 Hz), 3.9 (1 H, m), 7.65 (4 H, m), 7.95 (1 H, m), 8.47 (1 H, m), and 8.70 (2 H, m); $\nu_{max.}$ 2 210 cm^{-1}. Rearrangement was also conducted in degassed C_6D_6 at 254 °C (*k* 2.23 × 10^{-4} s^{-1}).

Thermolysis of (1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*ethynyl Phenyl Ketone* (**11**).—A mixture of the title compound (25 mg) in diphenyl ether (0.4 ml) was degassed (6 freeze–pump–thaw cycles) and the sealed tube was heated at 195 °C (50 min) and 217 °C (65 min). The product was chromatographed on silica (10 g) in dichloromethane–light petroleum (4:1) as eluant to give (1,3-*dimethyl*-1H-*cyclopenta*[l]*phenanthren*-2-*yl*)*ethynyl phenyl ketone* (**16**; X = C≡CCOPh) (10 mg), m.p. 181—187 °C (from ethanol) (Found: C, 90.35; H, 5.5%; M^+, 372.1505. $C_{28}H_{20}O$ requires C, 90.32; H, 5.4%; *M*, 372.1514); $\nu_{max.}$ 2 150 and 1 625 cm^{-1}; $\lambda_{max.}$ 405, 308, and 243 nm (ε 7 400, 6 200, and 15 500); δ_H(90 MHz) 1.66 (3 H, d, *J* 7 Hz), 2.98 (3 H, d, *J* 1.5 Hz), 4.10 (1 H, qm, *J* 7 Hz), and 7.4—9.0 (13 H, m); *m/z* 372, 252, 105, 91, 77, 55, and 44 (18, 6, 76.6, 100, 53.5, 18.2, and 75.5%). Approximate rate constants are: *k* (s^{-1}) 2.44 × 10^{-5} (167), 3.06 × 10^{-5} (170), 2.94 × 10^{-5} (173), and 4.46 × 10^{-5} (176.5 °C).

Thermolysis of (E)-{*Ethyl* 3-(1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*propenoate*} (**13**); R = CO_2Et).—The title compound (19 mg) was heated in degassed diphenyl ether (0.4 ml) at 117 °C in a sealed tube (8.5 h). The product was chromatographed on silica (10 g) in benzene as eluant to give *ethyl* 3-(1,3-*dimethyl*-1H-*cyclopenta*[l]*phenthren*-2-*yl*)*propenoate* [**16**; X = (*E*)-CH=CHCO$_2$Et] (17.5 mg), m.p. 170—172 °C (from benzene–light petroleum) (Found: C, 84.2; H, 6.65. $C_{24}H_{22}O_2$ requires: C, 84.2; H, 6.4%); $\nu_{max.}$ 1 697 and 1 610 cm^{-1}; $\lambda_{max.}$ 388, 306, 294sh, 282, 261, and 240.5 nm (ε 21 000, 16 600, 23 000, 24 400, 31 000, and 23 500); δ_H(90 MHz) 1.37 (3 H, t, *J* 8 Hz), 1.47 (3 H, d, *J* 7 Hz), 2.78 (3 H, d, *J* 1.5 Hz), 3.95 (1 H, qm, *J* 7 Hz), 4.33 (2 H, q, *J* 8 Hz), 6.07 (1 H, d, *J* 16 Hz), 7.95 (1 H, d, *J* 16 Hz), and 7.4—8.9 (8 H, m); *m/z* 342, 296, 253, 240, 126, 69, and 44 (100, 54.4, 100, 47, 19.3, 20.2, and 16.7%). Approximate first-order rate constant for rearrangement, *k* 7.44 × 10^{-5} s^{-1} (117 °C).

Thermolysis of (E)-2-(1,3-*Dimethyl*-1H-*cyclopenta*[l]*phenanthren*-1-*yl*)*vinyl Phenyl Ketone* (**13**; R = COPh).—The title compound (6 mg) was heated in degassed diphenyl ether (0.4 ml) at 110 °C (3 h) in a sealed tube. The product was chromatographed on silica (5 g) in benzene as eluant to give the *title compound* [**16**; X = (*E*)-CH=CHCOPh] (2 mg), m.p. 115—118 °C (from ethanol) (Found: M^+, 374.1671. $C_{28}H_{22}O$ requires *M*, 374.1671); $\nu_{max.}$ 1 645, 1 598, and 1 560 cm^{-1}; $\lambda_{max.}$ 429, 302, 256, and 246sh nm (ε 2 300, 3 100, 7 600, and 7 000). Approximate rate constant, *k* 1.5 × 10^{-4} s^{-1} (104.5 °C).

Acknowledgements

We thank the S.E.R.C. for financial support.

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Received 24*th October* 1985; *Paper* 5/1849