Condensed Cyclic and Bridged-ring Systems. Part 15.[1] Acid-catalysed Intramolecular Alkylations in 1-Diazoacetyl-1,2,3,4-tetrahydro-9-methoxy-1-methylphenanthrenes

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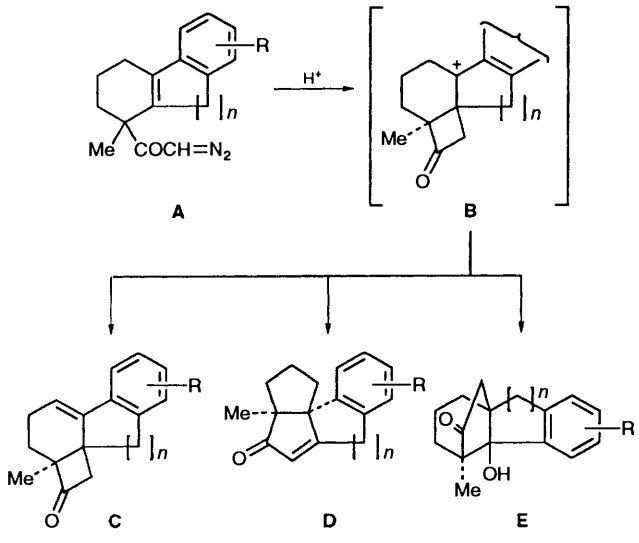
The acid-catalysed reaction of the 1-diazoacetyltetrahydrophenanthrene **1a** and the three new related diazoketones **1b–d** gave, in addition to the respective bridged ketones **2a–d** and the pentaleno annelated ketones **3a–d**, the acephenanthrones **4a–d**, which were also prepared in excellent yield by the rhodium(II) acetate-induced reaction of the diazoketones.

We have demonstrated[2–5] that in acid-catalysed intramolecular alkylations of the β,γ-unsaturated diazomethyl ketones **A**, there is an overwhelming preference for the formation of the respective cyclobutanone cation **B** through the participation of the π-bond in close proximity to the protonated diazocarbonyl centre, resulting in the unsaturated cyclobutanones **C**, the pentaleno annelated products **D** and the bridged hydroxycyclopentanones **E** in excellent yields (Scheme 1). Similar aryl



n = 1 or 2
R = H, OMe

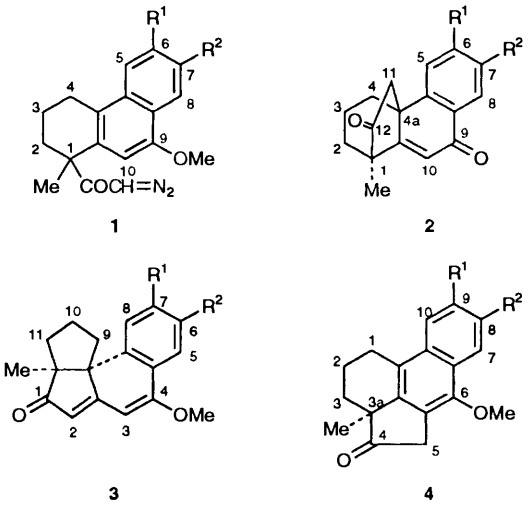
Scheme 1

bond participation in acid catalysed reactions of polycyclic hydroaromatic diazomethyl ketones have been reported recently.[6] The first example of an Ar_1-5 aryl participation was reported from these laboratories by Mukherjee and co-workers[7] in the acid-catalysed reaction of the tetrahydrophenthrene diazoketone **1a**. Thus, from the trifluoroacetic acid (TFA)-induced decomposition of compound **1a**, the Ar_1-5 product **2a** and the pentaleno ketone **3a** (the rearranged product through a cyclobutanone intermediate) were the only compounds isolated[7] in 28 and 44% yields, respectively. The formation of the aromatic ring alkylated ketone **4a** in that reaction, however, could not be ruled out.[6] As a consequence, it appeared necessary to reinvestigate the products from the acid-catalysed reaction of the diazoketone **1a**. It was also of considerable importance to evaluate the directive effects of the aromatic substituents on the mode of aryl participation in the intramolecular alkylations. Accordingly, three new hydrophenanthrene diazomethyl ketones **1b–d** were prepared and their intramolecular alkylations have been investigated in detail. We now report the outcome of these studies.

Results and Discussion

Initially, we repeated the cyclization of the diazoketone **1a** in CH_2Cl_2 with TFA, according to reported conditions,[7] to obtain a semisolid product which, on careful chromatography on silica gel, gave the known crystalline ketones **2a** (46%), **3a** (31%) and the new aromatic ring alkylated product **4a** (8%). The structure of acephenanthrone **4a** was established by direct comparison with an authentic sample prepared in 86% yield by the $Rh_2(OAc)_4$-catalysed insertion of the diazoketone **1a**[8].

In view of the interesting trichotomy of products, we decided to investigate this reaction in detail with the related diazoketones **1b–d**. The tetrahydrophenanthrene acids **9b–d**, the immediate precursors for compounds **1b–d**, were synthesized by a simple, general, converging route (Scheme 2) from the readily accessible tricyclic γ-lactones **5b**,[9] **5c**[10] and **5d**.[11] The keto lactones **6b**,[12] **6c** and **6d**, were prepared in excellent yield by oxidation of the respective lactones **5b**, **5c** and **5d**. They were then smoothly aromatized by treatment with NaH in benzene in the presence of a catalytic amount of methanol. The crude



a R^1 = H, R^2 = OMe
b R^1 = R^2 = H
c R^1 = OMe, R^2 = H
d R^1 = H, R^2 = Pr^i

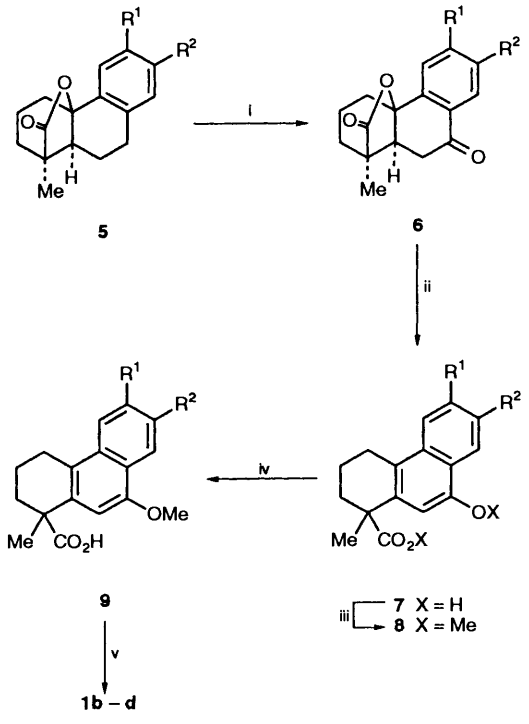
Throughout, the orientation of these structures may lead to an apparent inconsistency with the IUPAC rules on stereochemical nomenclature

Table 1 TFA-catalysed cyclization of diazoketones **1a–d**

Diazoketone	Products ratio[a] 2	3	4	Total yield (%)[b]
1a	**2a** (54)[c]	**3a** (36)[c]	**4a** (10)[c]	85
1b	**2b** (50)	**3b** (37)	**4b** (13)	70
1c	**2c** (12)	**3c** (29)	**4c** (59)	76
1d	**2d** (67)	**3d** (23)	**4d** (10)	83

[a] Determined by GLC. [b] Pure products (isolated). [c] Based upon the pure isolated products.

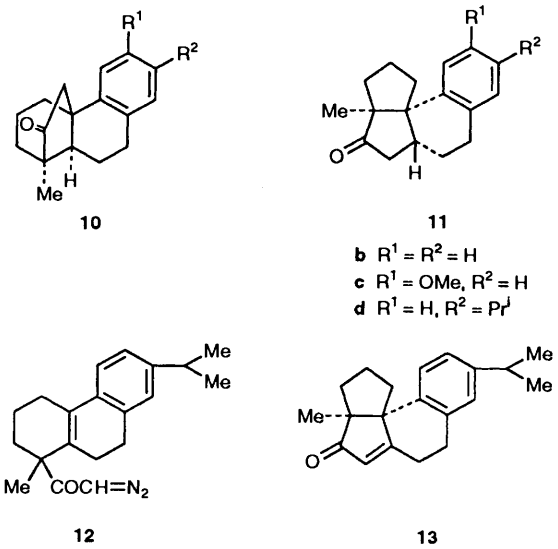
phenolic acids **7b–d**, were methylated with MeI in boiling acetone in the presence of anhydrous K_2CO_3 to afford the methoxy methyl esters **8b–d** in 70–75% yield. Attempted aromatization of the keto lactones **6b–d** by refluxing with KOH in ethylene glycol[12] followed by methylation of the dark phenolic acids **7b–d** gave compounds **8b–d** in only 40–45% yield. Saponification of each of the methoxy methyl esters **8b**, **8c** and **8d** furnished the respective acids **9b**, **9c** and **9d** as waxy solids, which were directly converted into the corresponding diazomethyl ketones **1b**, **1c** and **1d** following a standard procedure[2] (Scheme 2) in excellent overall yield.



Scheme 2 *Reagents:* i, CrO_3, AcOH, H_2O; ii, NaH, C_6H_6, MeOH; iii, MeI, K_2CO_3, MeCOMe; iv, KOH, $HOCH_2CH_2OH$; v, MeONa, $(COCl)_2$, C_6H_5N, C_6H_6; Et_3N, CH_2N_2–Et_2O

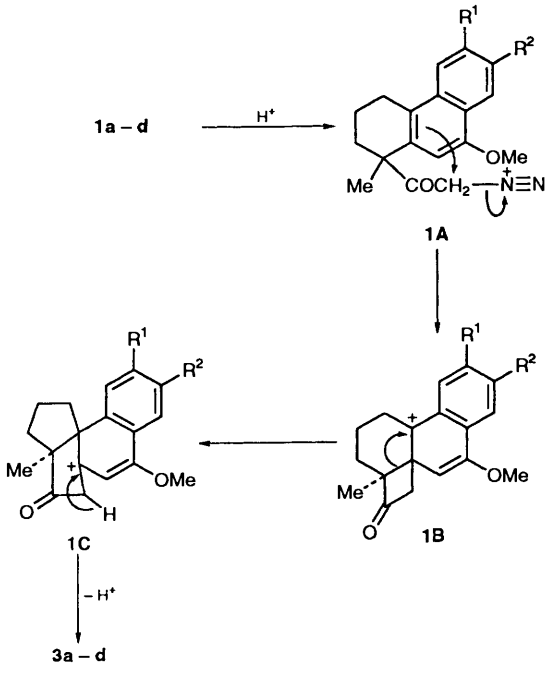
The decomposition of each of the diazoketones **1b–d** in CH_2Cl_2 at room temperature under $Rh_2(OAc)_4$ catalysis[8] gave the respective aromatic insertion products **4b–d**, as thick liquids in excellent yield. The efficiency of the rhodium(II) acetate in the facile formation of the strained 4-oxacephenanthrenes **4a–d** through highly regioselective aromatic ring insertion is noteworthy.

The cyclization[7] of the diazoketone **1b** in a dilute CH_2Cl_2 solution with TFA at −25 to −20 °C afforded a mixture of the bridged ketone **2b**, the pentaleno ketone **3b** and the acephenanthrone **4b** in a ratio of *ca.* 50:37:13 (GLC) in excellent yield along with a minor, unidentified compound. Careful chromatography of the product mixture gave compounds **2b** (32%), **3b** (28%) and **4b** (10%) the last of which was identical (mixed m.p., IR, ^1H NMR) with the sample prepared by $Rh_2(OAc)_4$ catalysed insertion of the diazoketone **1b**. Final confirmation of the structures came when compounds **2b** and **3b** were converted into the known ketones **10b**[13] and **11b**[4] through catalytic hydrogenation under acidic conditions in the presence of Pd–C (10%). Similarly, the TFA-catalysed cyclization of the diazoketone **1c** furnished a mixture of the ketones **2c**, **3c** and **4c** in a ratio of *ca.* 12:29:59 (GLC), in addition to a minor unidentified compound. Chromatographic separation of this mixture gave the semi-solid bridged ketone **2c** (9%), the pentaleno ketone (22%) and the acephenantherone **4c** (45%), the last of which was identical (mixed m.p., IR and ^1H NMR) with the sample described earlier. The spectral and analytical data of compounds **2c** and **3c** agree with the assigned structures which were finally established by catalytic hydrogenation of the compounds to the known ketones **10c**[10] and **11c**.[4] Finally, the diazoketone **1d**, on cyclization with TFA, gave the bridged ketone **2d**, the pentaleno ketone **3d** and the acephenanthrone **4d** in a ratio of *ca.* 67:23:10 (GLC), in addition to two other minor unidentified products. Chromatographic separation afforded compounds **2d** (55%), **3d** (19%) and **4d** (9%), the last of which was identical (IR and ^1H NMR) with the ketone obtained by $Rh_2(OAc)_4$-catalysed insertion of compound **1d**. The structure of the bridged ketone **2d** was confirmed by the transformation to the known ketone **10d**[11] by catalytic hydrogenation. The structure of compound **3d** was established by its stereospecific reduction, under acidic conditions, to the tetracyclic ketone **11d**, which was identical (IR and ^1H NMR) with a sample prepared through the catalytic reduction of the unsaturated ketone **13**, obtained by TFA–$HClO_4$-catalysed cyclization of the diazoketone **12** in CH_2Cl_2 by a standard method.[4]



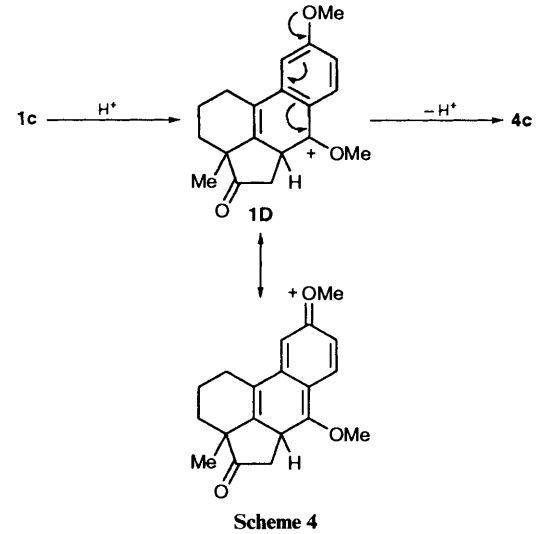
From the results of the TFA-catalysed reactions of the diazoketones **1a–d** (Table 1) it is clear that irrespective of the nature of the aromatic substituents in compounds **1a–d**, the Ar_1-4 participation[6] by the protonated diazocarbonyl group constitutes a substantial pathway in the acid-catalysed reaction. This, as has been frequently observed in π-bond[2–5] (cf. Scheme 1) and aromatic bond participations in such processes, is due to a favourable steric arrangement and results in the rearranged pentaleno ketones **3a–d** in moderate to good yield through the sequence **1A** ⟶ **1B** ⟶ **1C** (Scheme 3).

Although the electron donating C-9 methoxy group is favourably disposed in all the diazoketone substrates **1a–d** for an Ar_1-5 participation,[6,14] this pathway seems to be highly dependent upon the position of the electron donating substituent on the aromatic ring, affecting the electron density at



Scheme 3

the C-4a centre in the reactants. Thus, in the C-7 methoxy, the isopropyl substituted and the unsubstituted diazoketones **1a**, **1d** and **1b**, respectively, where electron density at C-4a is favourable,[15] the Ar_1-5 pathway is dominant in the acid-catalysed reaction, producing the corresponding bridged ketones **2a**, **2d** and **2b** as the major products whilst the competitive aromatic alkylation to form the ketones **4a**, **4d** and **4b** is the minor pathway. In contrast, the resonance stabilization * of the cation **1D** (Scheme 4), formed by insertion into the 9–10 π bond of the protonated diazocarbonyl function in compound **1c**, accounts for the major path leading to the ketone **4c**.



Scheme 4

Experimental

The compounds described are all racemates. M.p.s and b.p.s are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a Perkin-Elmer model PE 298 instrument. ^1H NMR spectra were recorded at 200 MHz on an XL-200 spectrometer for solutions in $CDCl_3$ with $SiMe_4$ as internal standard; J values are given in Hz. Analytical GLC was performed on a Shimadzu GC-9A model with a flame-ionization detector employing a 1.5% OV-17 (6.5 ft × 0.25 in) column with N_2 as the carrier gas. Column chromatography was performed on neutral alumina (Brockmann Grade 1, of BDH, India) or silica gel [Glaxo Laboratory (India) Ltd.]. Light petroleum refers to fractions of b.p. 40–60 °C unless otherwise stated. Ether (Et_2O) refers to diethyl ether. Elemental analyses were performed by Mr. P. P. Bhattacharya and S. K. Sarkar of this laboratory.

(±)-1,2,3,4,4a,9β,10,10a-*Octahydro*-6-*methoxy*-1β-*methyl*-9-*oxophenanthrene*-1α,4aα-*carbolactone* **6c**.—To a well stirred solution of the lactone **5c**[10] (1 g, 3.67 mmol) in acetic acid (10 cm^3), a solution of CrO_3 (1.5 g) in acetic acid (15 cm^3) and water (5 cm^3) was added and the stirring was continued for a further 14 h at room temp. The mixture was then diluted with water (40 cm^3) and extracted with Et_2O (4 × 50 cm^3). The extract was washed thoroughly with 5% aqueous $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated. Column chromatography of the residue over silica gel (10 g) using Et_2O–light petroleum (2:9) as eluent gave the pure keto lactone **6c** (840 mg, 80%) as a white crystalline solid; m.p. 197 °C (from Et_2O–light petroleum) (Found: C, 71.2; H, 6.4. $C_{17}H_{18}O_4$ requires C, 71.31; H 6.34%); ν_{max}/cm^{-1} 1773 (lactone), 1690 (ketone) and 1600 (aromatic); δ 1.22 (3 H, s, C-Me), 1.64–2.70 (9 H, m), 3.72 (3 H, s, $ArOCH_3$), 7.04 (1 H, dd, J 8 and 2, 7-ArH), 7.14 (1 H, d, J 2, 5-ArH) and 8.01 (1 H, d, J 8, 8-ArH).

(±)-1,2,3,4,4a,9β,10,10a-*Octahydro*-7-*isopropyl*-1β-*methyl*-9-*oxophenanthrene*-1α,4aα-*carbolactone* **6d**.—The lactone **5d**[11] (1.0 g, 3.52 mmol) was converted, in the same way as described for the formation of **6c**, into the keto lactone **6d** which was obtained as a colourless solid (680 mg, 65%); m.p. 162 °C (Et_2O–light petroleum) (Found: C, 76.2; H, 7.2. $C_{19}H_{22}O_3$ requires C, 76.48; H, 7.43%); ν_{max}/cm^{-1} 1770 (lactone), 1685 (ketone) and 1610 (aromatic); δ 1.28 (6 H, d, J 6, CMe_2), 1.61 (3 H, s, CMe), 1.70–2.80 (10 H, m), 7.34 (1 H, s, 8-ArH) and 7.70–8.10 (2 H, m, 5, 6-ArH).

Methyl 1,2,3,4-*Tetrahydro*-9-*methoxy*-1-*methylphenanthrene*-1-*carboxylate* **8b**.—To an ice-cold stirred suspension of NaH (50% dispersion, in mineral oil; 6 g) in dry benzene (80 cm^3) containing 2–3 drops of MeOH under N_2, a solution of the keto lactone **6b**[9,12] (2 g, 7.81 mmol) in dry benzene was added dropwise. The mixture was stirred for an additional 2 h and then left overnight. The mixture was treated with MeOH to decompose the excess of NaH after which it was diluted with water (100 cm^3). The organic layer was separated and the aqueous layer was washed with benzene (2 × 25 cm^3), acidified with 6 mol dm^{-3} HCl and extracted with Et_2O (4 × 50 cm^3). The Et_2O fraction was then dried (Na_2SO_4) and evaporated to give the crude phenolic acid (1.75 g) **7b**; ν_{max}/cm^{-1} 3400br, 1700 and 1625. This was directly methylated by treating it with anhydrous K_2CO_3 (6 g), MeI (8 cm^3) in dry refluxing acetone (50 cm^3) for 6 h. After removal of the acetone, the mixture was diluted with water (50 cm^3) and extracted with Et_2O (4 × 50 cm^3). The extract was washed with 5% aqueous $NaHCO_3$ and water (2 × 25 cm^3), dried (Na_2SO_4) and evaporated. Column chromatography of the residue over silica gel (12 g) using Et_2O–light petroleum (1:9) as eluent gave the pure methyl ester **8b** (1.55 g, overall 70%), as a pale yellow gum (Found: C, 76.0, H, 7.3. $C_{18}H_{20}O_3$ requires C, 76.03, H, 7.09%); ν_{max}/cm^{-1} 1730 (ester), 1630 and 1610; δ 1.75 (3 H, s, CMe), 2.0–2.66 (4 H, m, 2- and 3-H), 3.13 (2 H, br s, benzylic H), 3.70 (3 H, s, CO_2Me), 4.03 (3 H, s, ArOMe), 6.70 (1 H, s, 10-ArH), 7.50–7.98 (3 H, m, ArH) and 8.50 (1 H, m, ArH).

* We thank a referee for this suggestion.

Methyl 1,2,3,4-*Tetrahydro*-6,9-*dimethoxy*-1-*methylphenanthrene*-1-*carboxylate* **8c**.—The keto lactone **6c** (2 g, 6.99 mmol) was converted in the same way as described for compound **6b** into the corresponding methoxy ester **8c** (1.58 g, overall 72%); m.p. 124 °C (Et_2O–light petroleum) (Found: C, 72.4; H, 6.9. $C_{19}H_{22}O_4$ requires C, 72.59, H, 7.05%); ν_{max}/cm^{-1} 1725 (ester), 1630 and 1615; δ 1.64 (3 H, s, CMe), 1.76–2.54 (4 H, m, 2- and 3-H), 3.05 (2 H, t, *J* 7, benzylic-H), 3.70 (3 H, s, CO_2Me), 3.96 (6 H, s, 2 × ArOMe) 6.50 (1 H, s, 10-ArH), 7.16 (1 H, dd, *J* 8 and 2, 7-ArH), 7.26 (1 H, d, *J* 2, 5-ArH) and 8.0 (1 H, d, *J* 8, 8-ArH).

Methyl 1,2,3,4-*Tetrahydro*-7-*isopropyl*-9-*methoxy*-1-*methylphenanthrene*-1-*carboxylate* **8d**.—The keto lactone **6d** (2 g, 6.71 mmol) was converted in the same way as described for **6b** into the corresponding methyl ester **8d** (1.64 g, overall 75%), as a pale yellow oil (Found: C, 77.0, H, 8.0. $C_{21}H_{26}O_3$ requires C, 77.27, H, 8.03%); ν_{max}/cm^{-1} 1725 (ester) and 1620; δ 1.33 (6 H, d, *J* 6, $CHMe_2$), 1.62 (3 H, s, CMe), 1.79–2.59 (4 H, m, 2- and 3-H), 2.62–3.0 (3 H, m, 4 and $CHMe_2$), 3.50 (3 H, s, CO_2Me), 3.90 (3 H, s, ArOMe), 6.46 (1 H, s, 10-ArH) and 7.03–8.0 (3 H, m, ArH).

Preparation of Diazomethyl Ketones **1b–d**: 1-*Diazoacetyl*-9-*methoxy*-1-*methyl*-1,2,3,4-*tetrahydrophenanthrene* **1b**.—A solution of the ester **8b** (1 g, 3.52 mmol) in ethylene glycol (15 cm^3) was refluxed under N_2 for 4 h with a solution of KOH (2 g) in water (2 cm^3). After work-up the aqueous alkaline layer was acidified with 6 mol dm^{-3} HCl and extracted with Et_2O (4 × 40 cm^3). The dried (Na_2SO_4) Et_2O layer was evaporated to give the acid **9b** (970 mg) as waxy solid; ν_{max}/cm^{-1} 1700 (CO_2H), 1625 and 1620. To a solution of the crude acid **9b** (970 mg) in MeOH (10 cm^3) was added dropwise a 10% solution of NaOMe in MeOH until the solution became alkaline (phenolphthalein indicator). MeOH was removed under reduced pressure and the residue dried *in vacuo* (90 °C, 8 mmHg) for 2 h. To a cold stirred suspension (0 °C) of the sodium salt in dry benzene (75 cm^3) containing dry pyridine (0.3 cm^3) was added dropwise oxalyl chloride (1.5 cm^3). After the reaction mixture had been kept at 0 °C for 30 min, at room temperature for 30 min and finally at 60 °C for 1 h the precipitated salt was filtered off and taken up in Et_2O (100 cm^3) and the resulting solution was added with stirring to an ice-cold Et_2O solution of diazomethane (from 4 g of *N*-methylnitrosourea) containing NEt_3 (1 cm^3). The reaction mixture was stored overnight after which the precipitated salt was filtered off and the evaporated yellow residue was filtered through a short column of neutral alumina (15 g) with Et_2O–light petroleum (2:5) as eluent to furnish the pure diazoketone **1b** (927 mg, overall 80%) as a yellowish liquid (Found: C, 73.2; H, 6.0; N, 9.9. $C_{18}H_{18}N_2O_2$ requires C, 73.45; H, 6.16; N, 9.52%); ν_{max}/cm^{-1}, 2110 (C=N=N) and 1630 (CO of $COCHN_2$); δ 1.46 (3 H, s, CMe), 1.62–2.12 (4 H, m), 2.97 (2 H, br, s, benzylic-H), 3.89 (3 H, s, ArOMe), 4.69 (1 H, s, $COCHN_2$), 6.39 (1 H, s, 10-ArH) and 7.36–8.10 (4 H, m, ArH).

1-*Diazoacetyl*-1,2,3,4-*tetrahydro*-6,9-*dimethoxy*-1-*methylphenanthrene* **1c**.—The methoxy ester **8c** (1 g, 3.18 mmol) was converted into the diazoketone **1c** (920 mg, overall 89%), in the same way as described for compound **1b** (Found: C, 70.2; H, 6.0; N, 8.4. $C_{19}H_{20}N_2O_3$ requires C, 70.35; H, 6.22; N, 8.64%); ν_{max}/cm^{-1} 2110 (C=N=N) 1630 and 1610; δ 1.52 (3 H, s, CMe), 1.60–2.02 (4 H, m), 3.06 (2 H, m, benzylic-H), 3.96 (6 H, s, 2 × ArOMe), 4.67 (1 H, s, $COCHN_2$), 6.50 (1 H, s, 10-ArH), 7.12 (2 H, m, ArH) and 8.02 (1 H, d, *J* 8, 8-ArH).

1-*Diazoacetyl*-1,2,3,4-*tetrahydro*-7-*isopropyl*-9-*methoxy*-1-*methylphenanthrene* **1d**.—The methoxy ester **8d** (1 g, 3.06 mmol) was converted in the same way as described for compound **1b** into the diazoketone **1d** (820 mg, 79%) (Found: C, 75.1; H, 7.0; N, 8.2. $C_{21}H_{24}N_2O_2$ requires C, 74.97; H, 7.19; N, 8.33%); ν_{max}/cm^{-1} 2115 (C=N=N) and 1635; δ 1.30 (3 H, s, CMe), 1.42 (6 H, d, *J* 6, $CHMe_2$), 1.68–3.10 (7 H, m), 3.92 (3 H, s, ArOMe), 4.72 (1 H, s, $COCHN_2$), 6.33 (1 H, s, 10-ArH) and 7.08–7.98 (3 H, m, ArH).

Rhodium(II)*Acetate-catalysed Reaction of Diazomethyl Ketones* **1a–d**: 1,2,3,3a-*Tetrahydro*-6,8-*dimethoxy*-3α-*methylacephenanthren*-4(5H)-*one* **4a**.—A solution of the diazoketone **1a** (100 mg, 0.3 mmol) in anhydrous methylene dichloride (10 cm^3) was added to a magnetically stirred suspension of a catalytic amount of $Rh_2(OAc)_4$ (20 mg) in dry methylene dichloride (10 cm^3) under N_2 for 1 h. The material was then concentrated and the residue was filtered through silica gel (7 g) with Et_2O–light petroleum (1:9) as eluent to furnish a yellowish solid (78.5 mg, 86%); m.p. 146–148 °C (Et_2O–light petroleum) (Found: C, 76.9; H, 6.5. $C_{19}H_{20}O_3$ requires C, 77.00; H, 6.80%); ν_{max}/cm^{-1} 1745, 1620 and 1590; δ 1.30 (3 H, s, CMe), 1.46–3.19 (6 H, m), 3.72 (δ_A) and 4.06 (δ_B) (2 H, ABq, *J* 16, $COCH_2$), 3.92 (3 H, s, ArOMe), 4.0 (3 H, s, ArOMe), 7.10 (1 H, dd, *J* 8 and 2, ArH), 7.26 (1 H, d, *J* 2, ArH) and 7.72 (1 H, d, *J* 8, ArH).

1,2,3,3a-*Tetrahydro*-6-*methoxy*-3aα-*methylacephenanthren*-4(5H)-*one* **4b**.—The $Rh_2(OAc)_4$-catalysed insertion of the diazoketone **1b** (200 mg, 0.68 mmol) was performed following the same procedure as described for compound **1a** and the product **4b** was obtained as yellowish solid (165 mg, 92%); m.p. 127 °C (from Et_2O–light petroleum) (Found: C, 81.0; H, 6.6. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%); ν_{max}/cm^{-1} 1740 (C=O), 1630 and 1600; δ 1.38 (3 H, s, CMe), 1.52–1.64 (1 H, m, 2-H), 2.04–2.22 (3 H, m, 2- and 3-H), 2.80–2.96 (1 H, m, 1-H), 3.12–3.28 (1 H, m, 1-H), 3.6 (δ_A) and 4.06 (δ_B) (2 H, ABq, *J* 20, $COCH_2$), 4.04 (3 H, s, ArOMe), 7.50–7.58 (2 H, m, ArH) and 7.80–8.08 (2 H, m, ArH).

1,2,3,3a-*Tetrahydro*-6,9-*dimethoxy*-3aα-*methylacephenanthrene*-4(5H)-*one* **4c**.—The $Rh_2(OAc)_4$-catalysed insertion of the diazoketone **1c** (100 mg, 0.30 mmol) was performed following the same procedure as described for compound **1a** and the product **4c** was obtained as a pale yellow solid (82 mg, 90%); m.p. 131 °C (Et_2O–light petroleum) (Found: C, 76.9; H, 6.6. $C_{19}H_{20}O_3$ requires C, 77.00; H, 6.80%); ν_{max}/cm^{-1} 1750 and 1625; δ 1.40 (3 H, s, CMe), 1.56–3.24 (6 H, m), 3.54 (δ_A) and 4.07 (δ_B) (2 H, ABq, *J* 20, $COCH_2$) 3.97 (3 H, s, ArOMe), 4.07 (3 H, s, ArOMe), 7.16–7.26 (2 H, m, ArH) and 8.16 (1 H, *J* 8, 7-ArH).

1,2,3,3a-*Tetrahydro*-8-*isopropyl*-3aα-*methylacephenanthrene*-4(5H)-*one* **4d**.—The $Rh_2(OAc)_4$-catalysed insertion of the diazoketone **1d** (70 mg, 0.2 mmol) was carried out following the same procedure as described for compound **1a** and the product **4d** was obtained as viscous oil (57 mg, 89%) (Found: C, 81.6; H, 7.7. $C_{21}H_{24}O_2$ requires C, 81.8; H, 7.86%); ν_{max}/cm^{-1} 1740 and 1625; δ 1.32 (3 H, s, CMe), 1.36 (6 H, d, *J* 6, $CHMe_2$), 1.60–3.20 (7 H, m), 3.52 (δ_A) and 3.98 (δ_B) (2 H, ABq, *J* 20, $COCH_2$), 4.06 (3 H, s, ArOMe), 7.50 (1 H, br s, 9-ArH), 7.88 (1 H, d, *J* 8, 10-ArH) and 8.0 (1 H, br d, 7-ArH).

Acid-catalysed Cyclization of the Diazomethyl Ketones **1a–d**. *Compound* **1a**.—The acid-catalysed reaction of the diazoketone **1a** was carried out following the literature procedure.[7] To a solution of the diazoketone **1a** (600 mg, 1.78 mmol) in dry methylene dichloride (50 cm^3) at −25 °C, trifluoroacetic acid (0.4 cm^3) was added. The mixture was stirred at this temperature until the IR absorption at 2100 cm^{-1} disappeared (*ca.* 15 min), after which it was treated with 5% aqueous $NaHCO_3$ (5 cm^3) and extracted with methylene dichloride (3 × 25 cm^3). The extract was dried (Na_2SO_4) and evaporated to leave a gummy mass (420 mg) which was column

chromatographed on neutral alumina (25 g) with Et_2O–light petroleum (1:9) as eluent. The initial fractions (2 × 30 cm^3) gave compound **4a** (8%), m.p. 146–148 °C, identical (mixed m.p., IR, NMR and GLC) with the sample described above. Subsequent fractions (4 × 30 cm^3) gave compound **3a** (31%) as solid; m.p. 181–183 °C (lit.,[7] m.p. 182–183 °C). The last portion of the eluent (5 × 30 cm^3) gave compound **2a** (46%) as light yellow solid; m.p. 141–142 °C (lit.,[7] m.p. 139–140 °C).

Compound **1b**: (±)-1,2,3,4-*Tetrahydro*-1β-*methyl*-1α,4aα-*ethanophenanthrene*-9,12-*dione* **2b**, (8bRS, 11aSR)9,10,11,11a-*Tetrahydro*-4-*methoxy*-11aβ-*methylpentaleno*[6a,1-a]*naphthalen*-1-*one* **3b** *and Compound* **4b**.—The cyclization of the diazoketone **1b** (600 mg, 2.04 mmol) was carried out under conditions identical with those described for compound **1a**. GLC analysis of the product showed the presence of compounds **2b**, **3b** and **4b** in a ratio of 50:37:13 by co-injection with pure samples obtained after separation. These were separated by column chromatography as described above. Initial fractions gave compound **4b** (54 mg, 10%); m.p. 127 °C identical (mixed m.p., IR, NMR and GLC) with the samples described above. Subsequent fractions gave compound **3b** (146 mg, 28%) as light yellow solid; m.p. 119 °C (Found: C, 81.9; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.17; H, 6.81%); ν_{max}/cm^{-1} 1660 (=C–C=O) and 1600; δ 1.28 (3 H, s, CMe), 1.48–1.84 (4 H, m, 11- and 12-H), 2.24–2.42 (2 H, m, 10-H), 3.98 (3 H, s, C=C–OMe), 5.84 (1 H, s, 3-H), 6.06 (1 H, s, 2-H), 7.26–7.50 (3 H, m, ArH) and 7.84 (1 H, br d, ArH). The last fraction gave compound **2b** (160 mg, 32%) as a colourless solid; m.p. 156 °C (Et_2O–light petroleum) (Found: C, 81.2; H, 6.57. $C_{17}H_{16}O_2$ requires C, 80.92; H, 6.39%); ν_{max}/cm^{-1} 1750 (bridged five-membered C=O), 1660 (=C–C=O) and 1600; δ 1.30 (3 H, s, CMe), 1.70–1.92 (4 H, m, 2- and 3-H), 2.02–2.18 (1 H, m, 4 H), 2.32–2.46 (1 H, m, 4-H), 2.48 (δ_A) and 3.10 (δ_B) (2 H, ABq, *J* 18, 11-H), 6.41 (1 H, s, 10-H), 7.40–7.72 (3 H, m, 5-, 6- and 7-ArH) and 8.30 (1 H, br d, 8-ArH).

Catalytic hydrogenation of **3b** *to* **11b**. A solution of the pentaleno ketone **3b** (20 mg, 0.075 mmol) in ethanol (15 cm^3) containing 70% $HClO_4$ (0.1 cm^3) was hydrogenated in the presence of 10% Pd–C (10 mg) for 6 h. The catalyst was filtered off and the filtrate was cautiously neutralized with solid $NaHCO_3$. The undissolved material was filtered off and the filtrate was concentrated to afford **11b** (16 mg, 89%) as solid. This was recrystallized from Et_2O–light petroleum and had m.p. and mixed m.p. 92 °C; identical in all respects (IR, ^1H NMR, GLC) with an authentic sample.[4]

Catalytic hydrogenation of **2b** *to* **10b**. The unsaturated bridged diketone **2b** (25 mg, 0.1 mmol) was hydrogenated in the same way as described for compound **3b** to give **10b** (21 mg, 89%) as a solid; m.p. and mixed m.p. 118 °C, identical in all respects (IR, ^1H NMR, GLC) with an authentic sample.[13]

Compound **1c**: (±)-1,2,3,4-*Tetrahydro*-6-*methoxy*-1β-*methyl*-1α,4aα-*ethanophenanthrene*-9,12-*dione* **2c**, (8bRS, 11aSR)-9,10,11,11a-*Tetrahydro*-4,7-*dimethoxy*-11aβ-*methylpentaleno*-[6a,1-a]*naphthalen*-1-*one* **3c** *and Compound* **4c**.—The acid-catalysed reaction of the diazoketone **1c** (600 mg, 1.85 mmol) was carried out following the procedure described for compound **1a** to give a mixture of products (455 mg); GLC analyses showed these to comprise compounds **2c**, **3c** and **4c** in a ratio *ca.* 12:29:59 by coinjection with the pure samples as obtained after separation. Chromatographic separation was also carried out as described for compound **1a**. The initial fractions gave compound **4c** as a solid (240 mg, 45%); m.p. 131 °C identical (mixed m.p., IR, NMR, GLC) with the sample described above. The following fractions gave compound **3c** (120 mg, 22%) (Found: C, 77.1; H, 6.7. $C_{19}H_{20}O_3$ requires C, 77.00; H, 6.80%); ν_{max}/cm^{-1} 1660 (=C–C=O) and 1600; δ 1.32 (3 H, s, CMe), 1.57–2.44 (6 H, m), 3.88 (3 H, s, C=COMe), 3.96 (3 H, s, ArOMe), 5.81 (1 H, s, 3-H), 5.96 (1 H, s, 2-H), 6.81 (1 H, dd, *J* 8 and 2, 6-ArH), 6.84 (1 H, br s, 7-ArH), 7.78 (1 H, d, *J* 8, 5-ArH). The third portion gave compound **2c** (47 mg, 9%) (Found: C, 76.3; H, 6.2. $C_{18}H_{18}O_3$ requires C, 76.57; H, 6.43%); ν_{max}/cm^{-1} 1745 (five-membered bridged C=O), 1660 (=C–C=O) and 1600; δ 1.30 (3 H, s, CMe), 1.76–1.92 (4 H, m, 2- and 3-H), 2.06–2.40 (2 H, m, 4-H), 2.48 (δ_A) and 3.04 (δ_B) (2 H, ABq, *J* 20, $COCH_2$), 3.94 (s, ArOMe), 6.32 (1 H, s, 10-H), 6.82 (1 H, d, *J* 2, 5-ArH), 7.02 (1 H, dd, *J* 8 and 2, 7-ArH) and 8.26 (1 H, d, *J* 8, 8-ArH).

Catalytic hydrogenation of **3c** *to* **11c**. The pentaleno ketone **3c** (200 mg, 0.07 mmol) was hydrogenated in the same way as described for compound **3b** to give **11c** (16 mg, 88%) as an oil, identical in all respects (IR, ^1H NMR, GLC) with an authentic sample.[4]

Catalytic hydrogenation of **2c** *to* **10c**. The unsaturated bridged diketone **2c** (30 mg, 0.1 mmol) was hydrogenated in the same way as described for compound **3b** to give **10c** (25 mg, 95%) as solid; m.p. and mixed m.p. 131 °C, identical in all respects (IR, ^1H NMR, GLC) with an authentic sample.[10]

Compound **1d**.—(±)-1,2,3,4-*Tetrahydro*-7-*isopropyl*-1β-*methyl*-1α,4aα-*ethanophenanthrene*-9,12-*dione* **2d**, (8βRS, 11aSR)-9,10,11,11a-*Tetrahydro*-6-*isopropyl*-4-*methoxy*-11aβ-*methylpentaleno*[6a, 1-a]*naphthalen*-1-*one* **3d** *and Compound* **4d**.—The acid-catalysed reaction of the diazoketone **1d** (450 mg, 1.34 mmol) was carried out following the same procedure as described for compound **1a** to give a mixture of products (370 mg) the GLC analysis of which showed the presence of compounds **2d**, **3d** and **4d** in a ratio of 67:23:10 respectively, by coinjection with the pure samples as obtained after separation. The mixture was separated by column chromatography on neutral alumina (15 g). The initial fraction gave compound **4d** (9%) as gummy oil identical (IR, NMR, GLC) with the sample described above. The middle fractions gave compound **3d** (76 mg, 19%) as gummy oil (Found: C, 81.6; H, 7.6. $C_{21}H_{24}O_2$ requires C, 81.76; H, 7.84%); ν_{max}/cm^{-1} 1660 (–C=C–C=O) and 1600; δ 1.28 (6 H, d, *J* 6, $CHMe_2$), 1.30 (3 H, s, CMe), 1.44–1.92 (5 H, m), 2.40 (1 H, m), 2.96 (1 H, q, *J* 6, $CHMe_2$), 4.04 (3 H, s, C=C–OMe), 5.87 (1 H, s, 3-H), 6.07 (1 H, s, 2-H), 7.30–7.70 (3 H, m, ArH). The last portion gave compound **2d** (223 mg, 55%) as gummy oil (Found: C, 81.3; H, 7.6. $C_{20}H_{22}O_2$ requires C, 81.60; H, 7.53%); ν_{max}/cm^{-1} 1750 (five-membered bridged –C=O), 1665 (=C–C=O), 1605; δ 1.28 (3 H, s, CMe), 1.30 (6 H, d, *J* 6, $CHMe_2$), 1.70–1.90 (4 H, m), 2.04–2.40 (2 H, m, 1-H), 2.44 (δ_A) and 3.07 (δ_B) (2 H, ABq, *J* 18, –CO–CH_2–), 3.84–4.0 (1 H, m, $CHMe_2$), 6.38 (1 H, s, 10-H), 7.35 (1 H, d, *J* 8, 5-ArH), 7.52 (1 H, dd, *J* 8 and 1, 6-ArH) and 8.14 (1 H, d, *J* 1, 8-ArH).

Catalytic hydrogenation of **2d** *to* **10d**. The unsaturated bridged diketone **2d** (25 mg, 0.09 mmol) was hydrogenated in the same way as described for compound **3b** to give **10d** (21 mg, 87%) as solid; m.p. and mixed m.p. 90 °C, identical in all respects (IR, ^1H NMR, GLC) with an authentic sample.[11]

Acid-catalysed Cyclization of Diazoketone **12**: (8bSR, 11aSR)-3,4,9,10,11,11a-*hexahydro*-6-*isopropyl*-11a,β-*methylpentaleno*[6a,1-a]*naphthalen*-1-*one* **13**. To an ice-cold stirred solution of the diazoketone **12** (250 mg, 0.81 mmol) in dry methylene dichloride (2 cm^3) was added dropwise a mixture of TFA (0.4 cm^3) and $HClO_4$ (70%, 0.1 cm^3) in dry methylene dichloride (10 cm^3) over 5 min. The mixture was stirred at room temp. for an additional 45 min to give, after work-up followed by column chromatography on neutral alumina (10 g) using Et_2O–light petroleum (1:9) as eluent, the pure ketone (139 mg, 62%) as a solid; m.p. 106 °C (Found: C, 85.4; H, 8.5. $C_{20}H_{24}O$ requires C, 85.66; H, 8.63%); ν_{max}/cm^{-1} 1660 (=C–C=O) and 1600; δ 0.90 (3 H, s, CMe), 1.24 (6 H, d, *J* 6 $CHMe_2$), 1.34 (1 H,

d, *J* 6) 1.50–2.38 (6 H, m), 2.66–3.18 (4 H, m), 6.04 (1 H, s, 2-ArH), 6.98 (1 H, br s, 5-ArH) and 7.14 (2 H, br s, ArH).

(2aRS,8bSR,11aSR)-2,2aα,3,4,9,10,11,11a-*Octahydro*-6-*isopropyl*-11a,β-*methylpentaleno*[6a,1-a]*naphthalen*-1-*one* **11d**. *A: Catalytic Hydrogenation of the Cyclopentaleno Ketone* **13**.—The unsaturated ketone **13** (20 mg, 0.07 mmol) was hydrogenated in the same way as described for compound **3b** to give **11d** (17 mg, 94%) as a viscous oil (Found: C, 85.4; H, 9.1. $C_{10}H_{26}O$ requires C, 85.05; H, 9.28%); ν_{max}/cm^{-1} 1725 (five-member –C=O) and 1605; δ 0.80 (3 H, s, CMe), 1.24 (6 H, d, *J* 8, $CHMe_2$), 1.40–2.96 (14 H, m), 6.98 (1 H, br s, 5-ArH), 7.08 (1 H, br d, 7-ArH), 7.17 (1 H, d, *J* 8, 8-ArH).

B: Catalytic hydrogenation of **3d**. The pentaleno ketone **3d** (20 mg, 0.064 mmol) was hydrogenated in the same way as described for compound **3b** to give **11d** (16 mg, 92%) as an oil; identical (IR, ^1H NMR, GLC) with the sample described above.

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