Condensed Cyclic and Bridged-ring System. Part 9.[1] Stereocontrolled Synthesis and *X*-Ray Structural Analyses of *cis*-3,4,4a,9,10,10a-Hexahydro-1,4a-ethanophenanthrene-2(1*H*),12-dione and *trans*-3,4,4a,9,10,10a-Hexahydro-3,4a-ethanophenanthrene-2(1*H*),12-dione

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The isomeric bridged diketones *cis*-3,4,4a,9,10,10a-hexahydro-1,4a-ethanophenanthren-2(1*H*),12-dione (5) and *trans*-3,4,4a,9,10,10a-hexahydro-3,4a-ethanophenanthren-2(1*H*),12-dione (6) have been synthesised by highly regioselective intramolecular aldol condensations through the stereochemically defined *cis*- and *trans*-2,2-ethylenedioxy-1,2,3,4,4a,9,10,10a-octahydrophenanthren-4a-ylacetaldehydes (3f) and (4f) and their structures have been established by *X*-ray analysis. The isomeric diketones (5) and (6) undergo cleavage with toluene-*p*-sulphonic acid in boiling benzene leading finally to the known keto-ester (3a) and a new spiro-keto acid (14). Carbon-13 n.m.r. spectra of these and the other compounds reported in this paper have been measured and assigned.

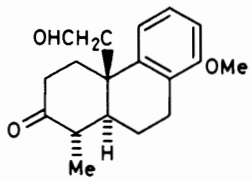
Intramolecular aldol condensation of the *trans*-octahydrophenanthrene keto-aldehyde (1) (or the related substrates) has been found to give either solely [2] or predominantly [3] the C-3 bridged ketols (2), depending upon the reaction conditions. However, the relative influence of the ring junction stereochemistry of the epimeric *cis*- and *trans*-hydrophenanthrene derivatives, for example (3g) and (4g), on the regioselectivity in such cyclisation has not previously been evaluated. To probe the possible stereochemical influence of the ring junction in (3g) and (4g) on the regioselectivity of intramolecular aldol condensation as well as to explore the synthetic utility of this reaction for model studies towards some complex diterpenoids [4] the present work was undertaken. This paper constitutes a detailed account of our studies concerning the stereochemically defined synthesis of the epimeric *cis*- and *trans*-acetal aldehydes (3f) and (4f) leading finally to the isomeric bridged diketones (5) and (6) through highly regioselective intramolecular aldol condensation.

Results and Discussion

The epimeric acetal aldehydes (3f) and (4f) were prepared *via* stereocontrolled routes from the known keto-lactone (7) [5] and the unsaturated keto-ester (8).[5] Catalytic hydrogenation of (8) in pyridine [6] over palladium–charcoal (10%) gave practically the pure *cis*-epimer (3a) in 95% yield. Hydrogenation of the lactone (7) in ethyl acetate in presence of ethanolic potassium hydroxide over 10% Pd–C followed by esterification of the resulting acid with diazomethane gave (3a) in 67% yield. Repeating the catalytic reduction of (8) in *N*,*N*-dimethyl formamide [7] produced a mixture of (3a) and the *trans*- epimer (4a) in a ratio of 2 : 3 (g.l.c. and ^{1}H n.m.r.) from which pure (4a) could be isolated by chromatography. A number of other solvents were tried for the hydrogenation of (8) using both Pd–C (10%) and PtO_2 catalysts. In each case the mixture of (3a) and (4a) was obtained (see Experimental section). However, in a highly stereoselective route the *trans*-ester (4a) was obtained as the sole product in 70% yield by reduction of the dry lithium salt of the unsaturated keto-acid (9), prepared by reaction of the keto-lactone (7) with lithium methoxide in methanol, with lithium in liquid ammonia followed by esterification with diazomethane and Jones oxidation. The stereochemical outcome of the lithium–ammonia reduction of (9) leading only to the *trans*-product (4a) clearly indicates that carboxy assisted protonation [8] plays no role in this case.

To assign the stereochemistry to (3a) and (4a), initial attempts were made for their direct chemical conversions into the known [9] epimeric 4a-methyloctahydrophenanthrenes (12f) and (13f) respectively. With this as the objective, the epimeric esters (3a) and (4a) were transformed into their respective deoxo-acids (3b) and (4b) by a modified Wolff-Kishner reduction.[10] Attempted conversion of (3b) into (12f) *via* a modified Hunsdiecker decarboxylation [11] with lead tetra-acetate in the presence of iodine followed by reduction with zinc dust and acetic acid led only to an inseparable mixture of rearrangement products.

Our search for an alternative solution to this problem [12] prompted us to undertake the synthesis and homologation of the epimeric *cis*- and *trans*-acids (12b) and (13b), and their unequivocal stereochemical assignments through transformations to (12f) and (13f). Towards this objective, the key intermediate enone-ester (11) was prepared in 36% yield by the condensation of the known β-keto-ester (10) [13] with methyl vinyl ketone in the presence of Triton-B methoxide in methanol followed by treatment with toluene-*p*-sulphonic acid in boiling toluene according to the procedure of Oommen.[14] Catalytic hydrogenation of (11) over Pd–C (10%) in pyridine [6] gave a 2 : 1 mixture of the *cis*- and the *trans*-esters (12a) and (13a) from which the pure *cis*-isomer (12a) was isolated by fractional crystallisation. Repeating the hydrogenation in *N*,*N*-dimethylformamide [7] produced (12a) and (13a) in a ratio of 1 : 3 from which the pure *trans*-isomer (13a) could be easily separated (*ca.* 50% yield) by recrystallisation. The comparison of the stereochemical distribution of the *cis*- and *trans*-pro-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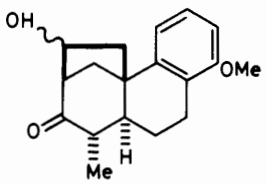
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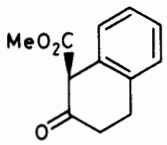
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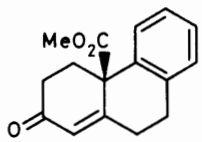
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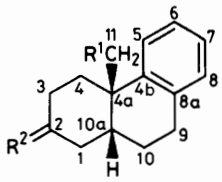
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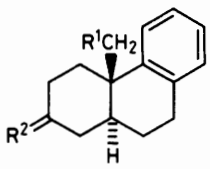
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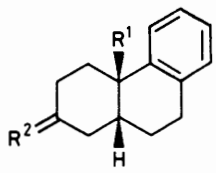
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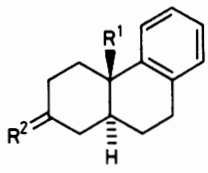
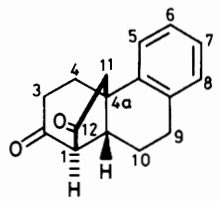

(13)

	R^1	R^2
a;	CO_2Me	O
b;	CO_2H	H_2
c;	CO_2Me	H_2
d;	CO_2Me	$O-[CH_2]_2-O$
e;	CH_2OH	$O-[CH_2]_2-O$
f;	CHO	$O-[CH_2]_2-O$
g;	CHO	O

	R^1	R^2
a;	CO_2Me	O
b;	CO_2H	H_2
c;	CO_2Me	H_2
d;	CH_2OH	H_2
e;	CHO	H_2
f;	CH_3	H_2
g;	$CH_2OSO_2CH_3$	H_2
h;	$COCHN_2$	H_2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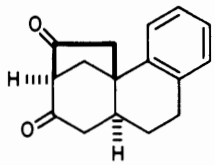
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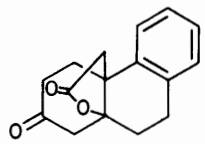
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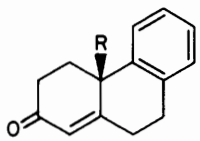

(8) R = CH_2CO_2Me
(9) R = CH_2CO_2H

ducts in catalytic hydrogenations of the enone-esters (8) and (11), incorporating an sp^3 and an sp^2 hybridised angular substituent respectively, shows that the former has a tendency to give more of the *cis*-product with respect to that of the latter. This result parallels that observed with the related angularly substituted octalone derivatives.[15] The stereoselectivity of these and similar reductions were found [16] to be extremely solvent and pH dependent and the results are not consistent with the ' haptophilicity ' argument of Thompson and coworkers.[17]

Modified Wolff-Kishner reduction of the *cis*- and the *trans*-keto-esters (12a) and (13a) afforded the corresponding deoxo-acids (12b) and (13b) in excellent yields. The stereochemical assignments of (12b) and (13b) have been made through the following sequence of transformations to the known epimeric hydrocarbons (12f) and (13f) respectively. Lithium aluminium hydride reduction of (12b) and (13b) afforded the respective alcohols (12d) and (13d) which were oxidised with pyridinium chlorochromate [18] to give the corresponding aldehydes (12e) and (13e) in good yields. Finally, Wolff-Kishner reduction [10] of (12e) and (13e) afforded the respective hydrocarbons (12f) and (13f), the ^1H n.m.r. spectral characteristics of which were identical with those reported in the literature [9] (see Experimental section).

With the stereochemistry of (12b) and (13b) secured, we first attempted the homologation of the *trans*-isomer (13b) by a displacement reaction of the crude mesylate (13g), prepared from the carbinol (13d) with sodium cyanide in hexamethylphosphoric triamide according to Gula and Spencer.[15] It gave a complex mixture from which no useful product could be isolated.

In a more direct route for homologation, the epimeric acids (12b) and (13b) were transformed to their respective diazomethyl ketones (12h) and (13h) in excellent yields *via* the sequential treatment of their dry sodium salts with oxalyl chloride in benzene and an excess of diazomethane in ether in the presence of triethylamine, following a standard method.[4,19] An attempted Arndt-Eistert reaction [20] of (12h) and (13h) using silver oxide or silver benzoate–triethylamine in methanol gave a complex mixture of products. These results were not altogether surprising. Hindered α-diazomethyl ketones have often been reported [21,22] to produce side-products arising from carbenoid or organometallic species along with the normal homologation products in conventional Arndt-Eistert reactions. On the other hand, photoinduced Wolff rearrangement of a few hindered α-diazomethyl ketones has been successfully used [22–24] for homologation without substantial side-reactions. It was gratifying to see that irradiation of the diazomethyl ketones (12h) and (13h) in methanol using a medium-pressure Hanovia lamp in a quartz vessel afforded the desired homologated methyl esters (3c) and (4c) in 70% yield as the only isolable products. These, on alkaline hydrolysis, gave the corresponding acids (3b) and (4b), identical with the aforementioned samples prepared through the keto-esters (3a) and (4a).

With the establishment of the stereochemistry of (3a) and (4a) the final stage was now set for their further transformations. Each of the epimeric keto-esters (3a) and (4a) was converted into their respective acetal esters (3d) and (4d) by using standard procedure,[10] which on reduction with lithium aluminium hydride afforded the acetal alcohols (3e) and (4e) in excellent overall yield. Oxidation of (3e) and (4e) with

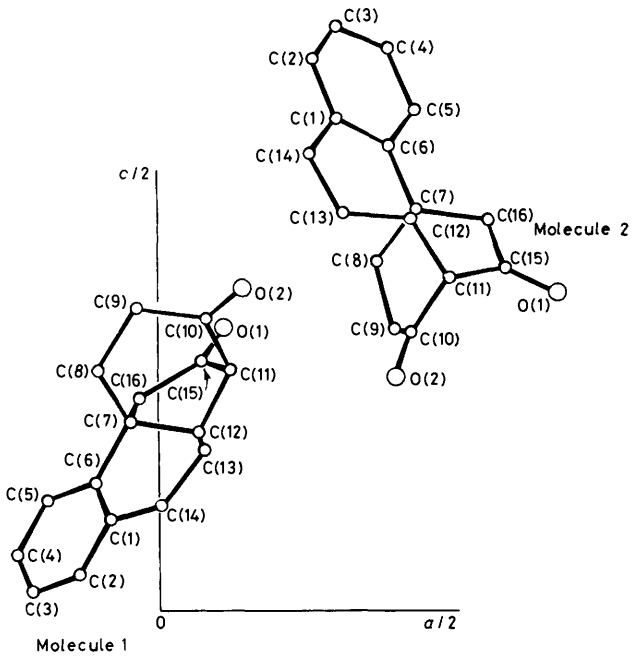


Figure 1. Perspective view of the *cis*-diketone (5) showing the crystallographic numbering scheme used

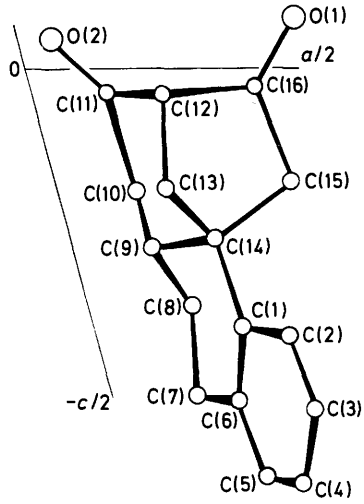
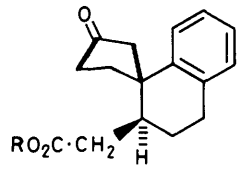


Figure 2. Perspective view of the *trans*-diketone (6) showing the crystallographic numbering scheme used



(14) R = H
(15) R = Me

pyridinium chlorochromate in methylene chloride [18] under controlled conditions gave the desired acetal aldehydes (3f) and (4f). Attempted deacetalation of (3f) and (4f) to their respective keto-aldehydes (3g) and (4g) even under mild acidic conditions led to concomitant aldol cyclisations. Under optimal conditions,[25] treatment of the *cis*-epimer (3f) with aqueous acetic acid (90%) at 80 °C for 3 h and then at room temperature overnight afforded a clean mixture of the intermediate bridged ketols which on direct oxidation with Jones reagent gave (5) along with presumably the corresponding C-3 regioisomer (not isolated) in a ratio of *ca.* 80—90 : 20—10 (g.l.c.). The crystalline diketone (5) was easily separated (65% yield) from this mixture. The *trans*-epimer (4f) under an identical reaction sequence gave a single crystalline diketone (6) (g.l.c.) in 81% yield. The spectral and analytical data of (5) and (6) are consistent with the assigned structures.

The complete structure and stereochemistry of each of these isomeric diketones (5) and (6) has been determined by *X*-ray crystal structure analysis and their perspective drawings are shown in Figures 1 and 2. It should be noted that the asymmetric unit of the *cis*-diketone (5) contains two crystallographically independent molecules in different orientations where the planes of the aromatic rings of the two molecules make an angle of 83° with each other.

Finally, an attempted isomerisation [26] of the *cis*-diketone (5) on treatment with toluene-*p*-sulphonic acid in boiling benzene gave a keto-acid through cleavage of the cyclopentanone ring which was characterised by its conversion (diazomethane) into the known keto-ester (3a). The *trans*-diketone (6) under identical conditions, on the other hand, gave the spiro keto acid (14) in excellent yield *via* the cleavage of the cyclohexanone ring. The spectral and analytical data of (14) and the corresponding methyl ester (15) are consistent with the assigned structures.

The present results indicate that intramolecular aldol condensation of the intermediate keto-aldehydes (3g) and (4g) (or the enolates) generated by acid catalysis from the *cis*- and *trans*- acetal aldehydes (3f) and (4f) proceeds preferentially through the enolisation of C-1 and C-3 (corresponding to C-4 and C-2 in steroids) respectively, analogous to that observed [27] in the reactions of A/B *cis*- and *trans*-3-oxo-steroids.

In order to examine the effects of the C-4a angular substituents in the chemical shifts in the *cis*- and *trans*-octahydrophenanthrene derivatives synthesised in the present work, the carbon shielding data for compounds (3a), (3c), (3e), (4a), (4c), (4e), (5), (6), (12a), (12c—f), (13a), (13c—f), and (14) are collected in Table 1. For each compound, both PND and SFORD spectra were recorded in addition to single frequency low-power decoupled spectra by setting the decoupler at different frequencies of the proton absorption region to assign unequivocally the chemical shifts to various non-aromatic carbons. The aromatic methine and non-protonated carbon chemical shifts were designated in analogy [28,29] with the assignments reported for structurally similar systems.

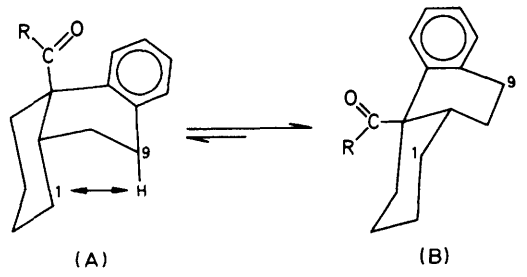
It can be seen from Table 1 that *cis*- and *trans*-octahydrophenanthrene derivatives can be distinguished from the chemical shift of C-11 of the angular substituent irrespective of its sp^3 or sp^2 hybridised nature. Thus, when the substituents are of type CH_2R (R = H, OH, CH_2OH, or CO_2Me), C-11 resonated downfield by 7—11 p.p.m. in the *cis*-isomer relative to that of the corresponding *trans*-compounds analogous to that reported for decalins [30] and androstanes,[31] while the effects of only 1.5—2.5 p.p.m. were observed if C-11 is in the sp^2 hybridised state (CHO or CO_2Me). Though C-10a of (12f) having an angular methyl substituent experienced very little (1 p.p.m.) upfield shift relative to that of the *trans*-isomer (13f), other *cis*-epimers (3a), (3c), (12a), (12c—e) exhibited significant shielding of their C-10a signal by 3.0—7.5 p.p.m. compared with that of their *trans*-counterparts, the effects being of smaller magnitude (3.0—4.5 p.p.m.) in the 2-oxo derivatives due to change in the ring conformation. A consistent upfield shift of the aromatic non-protonated carbon (C-4b) signal by

Table 1. ^{13}C chemical shifts *

Compd.	C-1	C-2	C-3	C-4	C-4a	C-4b	C-5	C-6	C-7
(3a)	43.1	210.6	37.8	34.6	39.6	138.7	125.8	126.6	126.3
(3c)	27.9	24.1	22.5	35.4	40.6	141.2	125.7	125.9	125.7
(3e)	36.4	109.1	31.1	31.6	39.0	140.0	125.6	125.9	125.9
(4a)	44.2	209.5	38.0	33.8	38.6	141.3	125.2	126.7	125.6
(4c)	29.2	26.1	22.1	34.3	39.5	143.7	124.8	126.0	125.4
(4e)	37.9	108.6	31.0	31.0	37.5	144.9	124.7	125.8	125.2
(5)	69.3	208.7	36.8	36.0	42.6	142.0	125.8	126.8	126.0
(6)	43.9	209.1	66.5	41.9	43.7	139.0	125.2	126.8	126.6
(12a)	44.7	209.8	38.6	34.3	50.3	137.1	126.3	127.0	126.5
(12c)	29.0	23.4	21.5	34.0	51.1	138.7	125.9	126.9	126.3
(12d)	27.9	24.0	22.3	32.6	43.2	139.4	125.8	126.3	125.8
(12e)	28.5	22.5	22.0	31.1	54.6	137.2	126.2	128.0	126.9
(12f)	28.2	24.5	23.0	38.2	37.5	144.2	125.0	125.8	125.8
(13a)	45.3	209.4	39.1	35.6	48.8	137.0	125.9	127.2	126.8
(13c)	30.2	26.1	24.1	37.0	50.0	139.3	125.5	126.6	126.6
(13d)	29.3	26.4	22.1	32.4	41.3	143.0	125.1	126.0	125.8
(13e)	30.2	25.6	23.3	33.0	53.6	138.1	126.2	127.0	126.6
(13f)	29.2	26.6	22.5	37.9	36.9	148.1	124.4	125.4	125.2
(14 †)	43.2	178.8	35.5	29.9	44.9	139.4	126.1	127.2	126.7

Compd.	C-8	C-8a	C-9	C-10	C-10a	C-11	C-12	OMe
(3a)	129.8	135.5	25.4	23.8	38.7	45.8	171.0	51.3
(3c)	129.5	136.1	26.5	25.0	37.6	46.9	171.9	51.0
(3e)	129.7	135.8	25.4	23.2	36.9	45.3	58.8	—
(4a)	129.5	135.2	28.3	24.9	43.2	36.5	171.8	51.2
(4c)	129.2	135.7	28.1	25.2	42.9	36.9	172.8	50.9
(4e)	129.4	135.9	27.8	24.4	40.0	32.4	59.1	—
(5)	129.5	134.3	27.9	20.1	48.0	49.0	202.5	—
(6)	129.4	136.5	29.6	25.7	42.7	49.2	200.9	—
(12a)	129.6	134.6	28.7	25.2	39.1	175.3	—	52.4
(12c)	129.3	135.6	29.0	24.7	36.3	176.4	—	51.9
(12d)	129.6	137.4	26.5	25.2	35.2	71.0	—	—
(12e)	129.8	135.0	28.8	24.2	34.3	203.1	—	—
(12f)	129.2	135.6	27.1	25.1	41.3	31.8	—	—
(13a)	129.5	136.9	29.2	25.5	42.3	173.4	—	52.0
(13c)	129.3	137.6	29.2	26.3	43.3	174.4	—	51.4
(13d)	129.5	136.8	28.8	25.5	41.7	63.6	—	—
(13e)	129.6	135.7	29.6	26.3	41.8	201.6	—	—
(13f)	129.2	135.4	29.4	25.9	42.3	21.7	—	—
(14 †)	129.0	136.4	28.6	26.4	38.3	52.6	217.6	—

* Spectra were recorded in $CDCl_3$ and the chemical shifts are expressed in the δ scale with $SiMe_4$ as internal standard. † For ease of comparison of data, the numbering system of octahydrophenanthrene derivative (6) from which it was derived, has been retained.



(A) (B)

2.5—5.0 p.p.m. was observed in *cis*-compounds which possess a CH_2R type angular substituent, (3a), (3c), (3e), (12d), and (12f), as against those in the *trans*-isomers, while compounds containing CHO or CO_2Me as the substituent, (12a), (12c), and (12e), showed an upfield shift for their C-8a signal of 2.3, 2.0, and 0.7 p.p.m. respectively relative to those of their *trans*-counterparts. This behaviour indicated, presumably, some sort of electronic interaction between the substituent and the aromatic ring. Besides, these three *cis*-compounds (12a), (12c), and (12e) also exhibited a downfield shift of their C-9 signal (δ 28.7—29.0 p.p.m.) compared with those (δ 25.4—27.1 p.p.m.) of other compounds (3a), (3c), (3e), (12d), and (12f) of the same series.

It is therefore reasonable to assume that due to the repulsive interaction between the closely spaced C=O and the aromatic π-electron system in conformer (A) (steroidal conformation), the three compounds (12a), (12c), and (12e) are expected to exist in the equilibrium mixture predominantly in the non-steroid conformation (B) in which C-9 is not involved in a γ_g (*γ-gauche*) interaction with C-1 resulting in the downfield shift of their C-9 signal. This also explains why these three compounds exhibited upfield shifts of their C-8a signal rather than C-4b contrary to observation in case of other compounds of the same series.

Experimental

The compounds described are all racemates. I.r. spectra of solids (KBr) and liquids (film) were recorded on a Perkin-Elmer model PE 298 spectrometer. U.v. spectra were recorded on a Beckmann DU Spectrophotometer for solutions in 95% ethanol. Unless otherwise specified ^1H n.m.r. spectra were recorded at 60 MHz on a Varian T-60A spectrometer in $CDCl_3$ solutions with tetramethylsilane as internal standard.

^{1}H N.m.r. (at 100 MHz) and ^{13}C n.m.r. spectra were recorded on a Jeol FX-100 FT n.m.r. spectrometer. Analytical g.l.c. was performed on a Hewlett Packard 5730A chromatograph equipped with a flame-ionisation detector (20 × $\frac{1}{8}$ in, 10% UCW-982 or 6 ft × $\frac{1}{8}$ in 3% SE-52) with N_2 as the carrier gas. Elemental analyses were performed by Mr. P. P. Bhattacharyya of this laboratory. Column chromatography was performed on neutral alumina (Brockman Grade 1). Petroleum and light petroleum refer to the fractions of b.p. 60—80 and 40—60 °C respectively. Ether refers to diethyl ether.

cis-*Methyl* 2-*Oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (3a).—*Method A*. The unsaturated keto-ester (8) (4 g, 14.8 mol) was hydrogenated in dry pyridine (80 ml) in presence of 10% Pd–C (350 mg) at room temperature and pressure. After the theoretical quantity of hydrogen had been consumed, the catalyst was filtered off and the solution diluted with ice-cold 2M-hydrochloric acid (600 ml) and then extracted with ether. The combined ethereal extracts were washed with water and dried (Na_2SO_4). Evaporation of the solvent afforded the saturated keto-ester (3a) (3.8 g, 95%) which was homogeneous (^{1}H n.m.r. and g.l.c.) and had m.p. 64 °C (ether–light petroleum) (Found: C, 74.8; H, 7.65. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%), $\nu_{max.}$ 1 710 cm^{-1}; δ 1.23—3.00 (m, 13H), 3.53 (s, 3 H, CO_2CH_3), and 7.03—7.20 (m, 4H, ArH).

Method B. To a solution of the keto-lactone (7) (850 mg, 3.32 mmol) in ethyl acetate (145 ml) was added a solution of KOH (0.209 g, 3.7 mmol) in ethanol (5 ml) and 10% Pd–C (110 mg). This mixture was stirred under an atmosphere of hydrogen. After the theoretical quantity of hydrogen had been consumed, the catalyst was removed by filtration. The filtrate was diluted with 1M-hydrochloric acid and the organic layer was separated. The aqueous layer after saturation with NaCl was extracted with ethyl acetate. Work-up followed by esterification with ethereal diazomethane afforded the aforementioned keto-ester (3a) (600 mg, 67%).

trans-*Methyl* 2-*Oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (4a).—*Method A*. A solution of the keto-lactone (7) (8 g, 32 mmol) in anhydrous methanol (250 ml) was refluxed under nitrogen for 4 h with an excess of LiOMe, prepared from LiH (0.72 g, 90 mmol) and methanol (10 ml). After removal of the solvent, the residue was freed from the last traces of methanol by distillation with benzene. This crude lithium salt of the keto-acid (9) was added to a well-stirred mixture of anhydrous liquid ammonia (500 ml) and THF (50 ml). Small pieces of Li were then added (1.4 g, 0.2 g-atom) during a 5-min period. Excess of solid ammonium chloride was added slowly and the ammonia was allowed to evaporate. After removal of THF the residue was carefully acidified with an excess of concentrated hydrochloric acid, and extracted with ethyl acetate. After removal of the solvent the crude acid was esterified with ethereal diazomethane to give a product which showed a strong OH band in its i.r. spectrum. This was dissolved in acetone and oxidised with Jones reagent [32] at 10—15 °C until the colour of the reagent persisted for 10 min; the mixture was then worked up. The crude product was chromatographed on neutral alumina. Elution with benzene–petroleum (1 : 1, v/v) afforded the *trans*-keto ester (4a) (6 g, 71% overall yield), m.p. 86 °C (ether–light petroleum) (Found C, 74.85; H, 7.5. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.4%), $\nu_{max.}$ 1 730 and 1 700 cm^{-1}; δ 1.30—3.06 (m, 13 H), 3.40 (s, 3 H, CO_2CH_3), and 7.05br (s, 4 H, ArH).

Method B. The unsaturated keto-ester (8) (4 g, 14.8 mmol) was hydrogenated in DMF (100 ml) in presence of 10% Pd–C (260 mg) at room temperature and pressure. The catalyst was filtered off and the filtrate diluted with water and then extracted with ether. Work-up of the extract afforded a colourless solid (4 g, 100%) which was found to be a mixture of the *cis*- and the *trans*-keto-esters (3a) and (4a) in a ratio of 40 : 60 by g.l.c. and ^{1}H n.m.r. spectroscopy. A part of the pure *trans*-isomer (*ca.* 1 g), m.p. and mixed m.p. 86 °C, with the sample described above, could be separated from this mixture by three recrystallisations from ether–light petroleum. The residual mixture on chromatography over neutral alumina afforded the pure *cis*-isomer (3a) (1.5 g) and the *trans*-epimer (4a) (1.1 g) by elution with light petroleum and benzene–petroleum (1 : 1) respectively.

The following hydrogenation conditions were also used to reduce the unsaturated keto-ester (8); the ratios of (3a) and (4a) obtained in each experiment as determined by g.l.c. analysis and relative peak intensities of the ^{1}H n.m.r. spectra, are given in parentheses: 10% Pd–C in ethyl acetate (46 : 56); 10% Pd–C in methanol (57 : 43); 10% Pd–C in ethanol (60 : 40); 10% Pd–C in acetic acid (44 : 56); PtO_2 in acetic acid (67 : 33); PtO_2 in ethyl acetate (80 : 20); 10% Pd–C in ethyl acetate–perchloric acid (55 : 45).

cis-1,2,3,4,4a,9,10,10a-*Octahydrophenanthrene*-4a-*ylacetic Acid* (3b).—The *cis*-keto-ester (3a) (1 g, 3.7 mmol) in diethylene glycol (30 ml) and 85% hydrazine hydrate (15 ml) was heated under a dry nitrogen atmosphere (a slow stream of N_2 was passed) for 1.5 h at 120—130 °C (graphite bath) with a continuous distillation system. After the solution had been cooled, KOH (2 g, 36 mmol) was added to it and the temperature raised to 210—220 °C; it was then kept at that temperature for 2.5—3 h. After the reaction mixture had been cooled it was poured onto ice–water (100 ml) and extracted with ether. Washings of the ether layer and the aqueous portion were acidified with 6M-hydrochloric acid and extracted with ether after saturation with sodium chloride. The ether extracts were washed with brine, dried, and solvent removed to yield the acid (3b) (850 mg, 95%) m.p. 110 °C (light petroleum) (Found: C, 78.5; H, 8.5. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%), $\nu_{max.}$ 1 695 cm^{-1}. The methyl ester (3c) was prepared by esterification with ethereal diazomethane; $\nu_{max.}$ 1 730 cm^{-1}; δ(CCl_4) 0.97—2.26 (m, 11 H, CH_2 and CH), 2.50 (s, 2 H, CH_2CO_2Me), 2.70—2.93 (m, 2 H, CH_2Ar), 3.50 (s, 3 H, CO_2CH_3), and 6.90—7.06 (m, 4 H, ArH).

trans-1,2,3,4,4a,9,10,10a-*Octahydrophenanthren*-4a-*ylacetic Acid* (4b).—The *trans*- keto-ester (4a) (1 g, 3.7 mmol) on reduction as described above afforded (4b) (800 mg, 89%), m.p. 102 °C (light petroleum) (Found: C, 78.55; H, 8.5. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%), $\nu_{max.}$ 1 685 cm^{-1}. The methyl ester (4c) was prepared by reaction of (4b) with ethereal diazomethane; $\nu_{max.}$ 1 730 cm^{-1}; δ(CCl_4) 1.23—3.00 (m, 15 H), 3.27 (s, 3 H, CO_2CH_3), and 6.93br (s, 4 H, ArH).

cis-*Methyl* 2,2-*Ethylenedioxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (3d).—A mixture of the keto-ester (3a) (2 g, 7.35 mmol) and ethylene glycol (1.25 ml, 22.4 mmol) in dry benzene containing toluene-*p*-sulphonic acid (100 mg) was refluxed for 20 h with a Dean-Stark water separator. The reaction mixture was cooled and poured into water (100 ml) containing KOH (50 mg). The benzene layer and two other extracts of the aqueous layer were washed with water, dried, and evaporated to give the acetal ester (3d) (2.0 g, 86%), m.p. 95 °C (ether–light petroleum) (Found: C, 72.0; H, 7.5. $C_{19}H_{24}O_4$ requires C, 72.12; H, 7.65%), $\nu_{max.}$ 1 725 cm^{-1}; δ 1.10—3.00 (m, 13 H), 3.56 (s, 3 H, CO_2CH_3), 3.90 (s, 4 H, OCH_2CH_2O), and 6.93—7.16 (m, 4 H, ArH).

trans-*Methyl* 2,2-*Ethylenedioxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (4d).—The *trans* keto-ester (4a) (2 g, 7.35 mmol) was treated under conditions identical with those described for the *cis*-isomer to give the acetal ester (4d) (2.0 g, 86%), m.p. 97 °C (ether–light petroleum) (Found: C, 72.0; H, 7.7. $C_{19}H_{24}O_4$ requires C, 72.12; H, 7.65%), $\nu_{max.}$ 1 725 cm^{-1}; δ 1.33—3.00 (m, 13H), 3.36 (s, 3 H, CO_2CH_3), 3.90 (s, 4 H, OCH_2CH_2O), and 7.03br (s, 4 H, ArH).

cis-2-(2,2-*Ethylenedioxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (3e).—A solution of the *cis* acetal ester (3d) (2 g, 6.33 mmol) in dry ether (50 ml) was added to a stirred slurry of lithium aluminium hydride (700 mg, 17.5 mmol) in dry ether (50 ml). After complete addition, the reaction mixture was refluxed for 4 h. Work-up afforded the *cis*-acetal alcohol (3e) (1.73 g, 95%), b.p. 140 °C (0.1 mmHg) (Found: C, 74.9; H, 8.4. $C_{18}H_{24}O_3$ requires C, 74.97; H, 8.39%), $\nu_{max.}$ 3 370 cm^{-1}; δ 1.00—2.60 (m, 12 H, CH_2, CH, and OH), 2.60—2.90 (m, 2 H, CH_2Ar), 3.53 (t, 2 H, *J* 7 Hz, CH_2OH), 3.86 (s, 4 H, OCH_2CH_2O), and 7.00—7.30 (m, 4 H, ArH).

trans-2-(2,2-*Ethylenedioxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (4e).—The *trans*-acetal ester (4d) (2 g, 6.33 mmol) was reduced in dry ether with lithiumaluminium hydride as above to give the *trans*-acetal alcohol (4e) (1.73 g, 95%), m.p. 128 °C (ether–light petroleum) (Found: C, 75.0; H, 8.4. $C_{18}H_{24}O_3$ requires C, 74.97; H, 8.39%), $\nu_{max.}$ 3 300 cm^{-1}; δ 1.33—2.56 (m, 12 H, CH_2, CH, and OH), 2.86 (m, 2 H, CH_2Ar), 3.93 (s, 4 H, OCH_2CH_2O), and 7.10br (s, 4 H, ArH).

cis-2,2-*Ethylenedioxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetaldehyde* (3f).—To a well-stirred ice-cold suspension of pyridinium chlorochromate (1g) in dichloromethane (10 ml) was added a solution of the *cis*-acetal alcohol (3e) (1 g, 3.47 mmol) in dichloromethane (6 ml). After being stirred for 2 h at 0 °C the reaction mixture was diluted with ether (30 ml) and the black precipitate repeatedly washed with ether. The combined ether layers were washed with 2% aqueous KOH, followed by water until free from alkali and then dried (Na_2SO_4). The solvent was removed to give the acetal aldehyde (3f) (0.9 g, 90%), b.p. 145 °C (0.2 mmHg) (Found: C, 75.3; H, 7.6. $C_{18}H_{22}O_3$ requires C, 75.49; H, 7.74%), $\nu_{max.}$ 1 700 cm^{-1}; δ 1.33—3.00 (m, 13 H, CH_2, CH), 3.83 (s, 4 H, OCH_2CH_2O), 7.00—7.16 (m, 4 H, ArH), and 9.53 (t, 1 H, *J* 3 Hz, CHO).

trans-2,2-*Ethylenedioxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetaldehyde* (4f).—The *trans*-acetal alcohol (4e) (1 g, 3.47 mmol) was oxidised with pyridinium chlorochromate (1 g) in dichloromethane (10 ml) as above to afford the *trans*-acetal aldehyde (4f) (0.9 g, 90%), b.p. 150 °C (0.1 mmHg) (Found: C, 75.4; H, 7.7. $C_{18}H_{22}O_3$ requires C, 75.49; H, 7.7%), $\nu_{max.}$ 1 715 cm^{-1}; δ 1.33—2.33 (m, 9 H, CH_2, CH), 2.57 (d, 2 H, *J* 3 Hz, CH_2CHO), 2.93 (t, 2 H, *J* 6 Hz, CH_2Ar), 7.13br (s, 4 H, ArH), and 9.43 (t, 1 H, *J* 3 Hz, CHO).

4a-*Methoxycarbonyl*-4,4a,9,10-*tetrahydrophenanthren*-2(3H)-*one* (11).—To a solution of the β-keto-ester (10) [13] (15 g, 73.5 mmol) in ice-cold anhydrous methanol (500 ml) under an atmosphere of nitrogen was added dropwise methyl vinyl ketone (6.2 g, 89 mmol). Triton B methoxide (1.71 g, 10 mmol) [40% solution of benzyl(trimethyl)ammonium methoxide in methanol] was then added and the reaction mixture cooled for 15 min; it was then set aside at room temperature for 24 h. The progress of the reaction was followed by periodic testing with ferric chloride. A few drops of 10% acetic acid were then added to neutralize the solution. The methanol was evaporated under reduced pressure and the residue was diluted with water. Work-up with ether afforded a hydroxy-ester as indicated by i.r. and ^1H n.m.r. spectroscopy.

The crude product was refluxed with toluene-*p*-sulphonic acid (1 g) in dry toluene (250 ml) using a Dean-Stark water separator. After 16 h, the reaction mixture was evaporated to dryness and taken up in benzene. The benzene layer was washed with water, dried, and evaporated. The residual thick liquid on distillation afforded the unsaturated keto-ester (11) (10 g, 53%), b.p. 160 °C (0.1 mmHg); $\nu_{max.}$ 1 725, 1 660, and 1 625 cm^{-1}; $\lambda_{max.}$ 234 nm (log ε 4.04); δ(CCl_4) 1.23—3.06 (m, 8 H, CH_2), 3.63 (s, 3 H, CO_2CH_3), 5.83 (s, 1 H, COCH=C), and 6.96—7.33 (m, 4 H, ArH). The 2,4-dinitrophenylhydrazone had m.p. 225 °C (ethyl acetate) (Found: C, 60.75; H, 4.8; N, 13.2. $C_{22}H_{20}O_6N_4$ requires C, 60.54; H, 4.62; N, 12.84%).

cis-4a-*Methoxycarbonyl*-3,4,4a,9,10,10a-*octahydrophenanthren*-2(1H)-*one* (12a).—The unsaturated keto-ester (11) (2 g, 7.75 mmol) in dry pyridine (25 ml) was hydrogenated in the presence of 10% Pd–C (200 mg) at room temperature and pressure. The catalyst was filtered off and the mixture worked up as described for the reduction of (8), to give a yellowish product which was filtered through a short column of neutral alumina to afford a mixture (1.9 g, 95%) of *cis*- and the *trans*-epimers (12a) and (13a) in the ratio of 2 : 1 (^1H n.m.r.). Recrystallisation twice from light petroleum gave pure *cis*-epimer (12a) (1.1 g), m.p. 104 °C (Found: C, 74.6; H, 7.1. $C_{16}H_{18}O_3$ requires C, 74.39; H, 7.02%), $\nu_{max.}$ 1 725 and 1 715 cm^{-1}; δ 1.70—3.13 (m, 11H), 3.73 (s, 3 H, CO_2CH_3), and 7.1br (s, 4 H, ArH).

trans-4a-*Methoxycarbonyl*-3,4,4a,9,10,10a-*octahydrophenanthren*-2(1H)-*one* (13a).—The unsaturated keto-ester (11) (2 g, 7.75 mmol) on hydrogenation in DMF (50 ml) in the presence of Pd–C (10%) (130 mg) afforded a mixture of *cis*- and *trans*-epimers (1.8 g, 90%) (12a) and (13a), in a ratio of 1 : 3 (^1H n.m.r.) after filtration of the crude product through a short column of neutral alumina. Recrystallisation twice from ether–light petroleum (1 : 1) gave the pure *trans*-isomer (13a) (1 g), m.p. 118 °C (Found: C, 74.5; H, 7.2 $C_{16}H_{18}O_3$ requires C, 74.39; H, 7.02%), $\nu_{max.}$ 1 725 and 1 710 cm^{-1}; δ 1.47—3.23 (m, 11H), 3.60 (s, 3 H, CO_2CH_3), and 7.00—7.43 (m, 4 H, ArH).

cis-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene*-4a-*carboxylic Acid* (12b).—The *cis*-keto-ester (12a) (1 g, 3.87 mmol) and 85% hydrazine hydrate (15 ml) in diethylene glycol (30 ml) was heated under a dry N_2 atmosphere for 1.5 h at 120—130 °C (graphite bath). The reaction mixture was cooled and KOH (2 g, 36 mmol) was added and the mixture then heated to 210—220 °C for 2.5—3 h. Work-up as described earlier afforded (12b) (800 mg, 89%), m.p. 143 °C (light petroleum) (Found: C, 78.3; H, 8.1. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%), $\nu_{max.}$ 1 685 cm^{-1}. The methyl ester (12c) was prepared by reaction of the acid (12b) with ethereal diazomethane; $\nu_{max.}$ 1 725 cm^{-1}; δ(CCl_4) 1.23—2.60 (m, 11H), 2.80 (t, 2 H, *J* 6 Hz, CH_2Ar), 3.57 (s, 3 H, CO_2CH_3), and 7.00br (s, 4 H, ArH).

trans-1,2,3,4,4a,9,10,10a-*Octahydrophenanthren*-4a-*carboxylic Acid* (13b).—The *trans* keto-ester (13a) (1 g, 3.87 mmol) was similarly subjected to Wolff-Kishner reduction to give the acid (13b) (830 mg, 93%), m.p. 162 °C (light petroleum) (Found: C, 78.25; H, 7.95. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%), $\nu_{max.}$ 1 685 cm^{-1}. The methyl ester (13c) was prepared by reaction of the acid (13b) with ethereal diazomethane; $\nu_{max.}$ 1 725 cm^{-1}; δ(CCl_4) 1.10—2.66 (m, 11 H, CH_2,CH), 2.66—

2.93 (m, 2 H, CH_2Ar), 3.53 (s, 3 H, CO_2CH_3), and 6.86—7.40 (m, 4 H, ArH).

cis-1,2,3,4,4a,9,10,10a-*Octahydrophenanthren*-4a-*ylmethanol* (12d).—A solution of the *cis*-acid (12b) (400 mg, 1.74 mmol) in dry ether (20 ml) was added to lithium aluminium hydride (400 mg, 10.50 mmol) in dry ether (25 ml) and refluxed for 5 h. After work-up the solvent was removed to yield the corresponding alcohol (12d) (350 mg, 93%), m.p. 48 °C. An analytical sample was prepared by distillation, b.p. 120—130 °C (0.15 mmHg) (Found: C, 83.2; H, 9.6. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%), $\nu_{max.}$ 3 360 cm^{-1}; δ(100 MHz) 1.00—2.28 (m, 12 H, CH_2, CH, OH), 2.68—2.96 (m, 2 H, CH_2Ar), 3.40—3.68 (m, 2 H, CH_2OH), and 7.04—7.36 (m, 4 H, ArH).

trans-1,2,3,4,4a,9,10,10a-*Octahydrophenanthren*-4a-*ylmethanol* (13d).—The *trans*-acid (13b) (700 mg, 3.04 mmol) in dry ether (50 ml) was reduced with lithium aluminium hydride (700 mg, 17.5 mmol) to give the corresponding alcohol (13d) (650 mg, 99%), m.p. 93 °C (light petroleum) (Found: C, 83.5; H, 9.4. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%), $\nu_{max.}$ 3 380 and 3 300 cm^{-1}; δ(100 MHz) 1.00—2.60 (m, 12 H, CH_2, CH and OH), 2.84—3.00 (m, 2 H, CH_2Ar), 3.58 (δ_A) and 3.69 (δ_B) (AB_q, 2 H, *J* 11 Hz, CH_2OH), and 6.94—7.36 (m, 4 H, ArH).

cis-1,2,3,4,4a,9,10,10a-*Octahydrophenanthren*-4a-*carbaldehyde* (12e).—To a stirred suspension of pyridinium chlorochromate (400 mg) in dichloromethane (10 ml) at 0 °C, the *cis*-alcohol (12d) (300 mg, 1.39 mmol) in dichloromethane (6 ml) was added and the stirring was continued for 2 h at 0 °C. Work-up as before followed by distillation of the residue at 85—90 °C (0.1 mmHg) afforded (12e) (250 mg, 83%), $\nu_{max.}$ 1 720 cm^{-1}; δ (CCl_4) 0.86—3.00 (m, 13 H), 7.03br (s, 4 H, ArH), and 9.06 (s, 1 H, CHO). The semicarbazone had m.p. 201 °C (methanol) (Found: C, 70.85; H, 8.1. $C_{16}H_{21}N_3O$ requires C, 70.82; H, 7.80%).

trans-1,2,3,4,4a,9,10,10a-*Octahydrophenanthren*-4a-*carbaldehyde* (13e).—The *trans*-alcohol (13d) (150 mg, 0.69 mmol) was oxidised with pyridinium chlorochromate (200 mg) in dichloromethane to afford the aldehyde (13e) (120 mg, 80%), b.p. 110—115 °C (0.1 mmHg), $\nu_{max.}$ 1 720 cm^{-1}; δ (CCl_4) 0.87—3.00 (m, 13 H), 6.79—7.17 (m, 4 H, ArH), and 8.86 (s, 1 H, CHO). The semicarbazone had m.p. 228 °C (decomp.) (methanol) (Found: C, 70.85; H, 7.8. $C_{16}H_{21}N_3O$ requires C, 70.82; H, 7.80%).

cis-4a-*Methyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene* (12f).—The *cis*-aldehyde (12e) (250 mg, 1.17 mmol) in diethylene glycol (8 ml) and hydrazine hydrate (4 ml) was heated at 120—130 °C (graphite bath) for 1.5 h, under a dry nitrogen atmosphere. To the cold reaction mixture, KOH (75 mg, 1.88 mmol) was added and the temperature raised and maintained at 210—220 °C for 2.5 h. Work-up afforded the hydrocarbon (12f) (200 mg, 85.6%). The CH_3 singlet at δ 1.23 along with complex multiplet at δ_H 1.00—2.46 (14 H, CH_2, CH), 2.63—2.96 (m, 2 H, CH_2Ar), and 6.93—7.33 (m, 4 H, ArH) [lit.,[9] 1.23 for the 4a-Me singlet in (12f)].

trans-4a-*Methyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene* (13f).—The *trans*- aldehyde (13e) (100 mg, 0.47 mmol) was similarly subjected to Wolff-Kishner reduction affording the hydrocarbon (13f) (75 mg, 84%). The CH_3 singlet at δ 1.07 along with the complex multiplet at δ 1.10—2.50 (14 H, CH_2, CH), 2.67—3.00 (m, 2 H, CH_2Ar), and 6.93—7.33 (m, 4 H, ArH) [lit.,[9] δ 1.07 for the 4a-Me singlet in (13f)].

trans-4a-*Methylsulphonyloxymethyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene* (13g).—A solution of the *trans*-keto alcohol (13d) (500 mg, 2.3 mmol) and dry pyridine (1.7 ml) in dry dichloromethane (10 ml) was kept at −10 to −7 °C and methanesulphonyl chloride (0.3 ml, 3.9 mmol) was added dropwise. The reaction mixture was set aside overnight at −10 °C. After dilution with water (20 ml), the reaction mixture was extracted with dichloromethane. The combined extracts were washed with water and dried and solvent removed. The residue was purified by passage through a short column of neutral alumina with benzene as eluant to give the mesylate (13g) (650 mg, 95%) as a colourless semisolid; $\nu_{max.}$ 1 450, 1 350, and 1 175 cm^{-1}; δ 1.00—2.23 (m, 11 H, CH_2 and CH), 2.47 (s, 3 H, OSO_2CH_3), 2.63—3.16 (m, 2 H, CH_2Ar), 4.21 (δ_A) and 4.58 (δ_B) (AB_q, 2 H, *J* 10 Hz, CH_2OSO_2), and 7.03—7.40 (m, 4 H, ArH).

cis-4a-*Diazoacetyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene* (12h).—The acid (12b) (200 mg, 0.86 mmol) in dry methanol (10 ml) was neutralised with a dilute solution of sodium methoxide in methanol with phenolphthalein as indicator. After removal of solvent the residue was freed from the last trace of methanol by repeated distillation with dry benzene. The dried sodio-salt was suspended in dry benzene (10 ml) containing pyridine (0.1 ml) and the suspension was cooled in an ice-bath and treated with oxalyl chloride (0.3 ml, 2.2 mmol). The mixture was stirred at 0 °C for 30 min and at room temperature for 30 min and finally warmed to 55—60 °C for 1 h. The precipitate was filtered off and the filtrate was concentrated under reduced pressure to afford the crude acid chloride, which was dissolved in dry ether (20 ml) and the solution added dropwise to a stirred solution of ice-cold ethereal diazomethane containing dry triethylamine (0.1 ml). The reaction mixture was left overnight at room temperature and then filtered. The filtrate was concentrated and the crude product was purified by filtration through a short column of neutral alumina (5 g) with ether–light petroleum (1 : 1, v/v) as eluant to yield the diazoketone (12h) (200 mg, 85%); $\nu_{max.}$ 2 100 and 1 625 cm^{-1}; δ 1.16—2.50 (m, 11 H, CH_2, CH), 2.76 (t, 2 H, *J* 6 Hz, CH_2Ar), 4.70 (s, 1 H, $COCH{=}N_2$), and 7.13br (s, 4 H, ArH).

trans-4a-*Diazoacetyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthrene* (13h).—The diazoketone (13h) (200 mg) was prepared in a manner similar to that described above from the *trans*-acid (13b) (200 mg); $\nu_{max.}$ 2 100 and 1 625 cm^{-1}, δ 1.33—2.56 (m, 11 H, CH_2, CH), 2.83 (t, 2 H, *J* 7 Hz, CH_2Ar), 4.86 (s, 1 H, $COCH{=}N_2$), and 7.10—7.26 (m, 4 H, ArH).

Photo-Wolff Rearrangement of the cis-*Diazomethyl Ketone* (12h) *to the Homologous* cis-*Ester* (3c).—The diazoketone (12h) (200 mg, 0.79 mmol) in dry methanol (200 ml) was irradiated with a 450-W Hanovia medium-pressure mercury vapour lamp in a quartz well. The progress of the reaction was monitored by disappearance of the diazoketone i.r. band at 2 100 cm^{-1}. After completion of the reaction (*ca.* 2—2.5 h), solvent was removed and the product chromatographed over neutral alumina, to afford the methyl ester (3c) (160 mg, 79%) identical with the sample described earlier (i.r. and ^1H n.m.r.). Saponification of a part of the ester (3c) with 5% methanolic KOH afforded the known acid (3b), m.p. and mixed m.p. 110 °C.

Photo-Wolff Rearrangement of the trans-*Diazomethyl Ketone* (13h) *to the Homologous* trans-*Ester* (4c).—The diazoketone (13h) (200 mg, 0.79 mmol) in dry methanol (200 ml) was subjected to a photo-Wolff rearrangement in a similar way to the *cis*-diazoketone (12h) to afford the *trans*-methyl ester (4c) (160 mg, 79%), identical with the sample described earlier (i.r. and

Table 2. Positional parameters ($\times 10^4$) of the non-hydrogen atoms of the asymmetric unit of the *cis*-diketone (5) (Figure 1) with their e.s.d.s

	x	*y*	*z*
Molecule 1			
C(1)	−926(4)	4 398(5)	1 047(3)
C(2)	−1 532(5)	4 529(5)	400(3)
C(3)	−2 404(6)	3 799(5)	204(4)
C(4)	−2 694(5)	2 892(5)	638(4)
C(5)	−2 088(5)	2 736(5)	1 288(3)
C(6)	−1 205(4)	3 481(4)	1 489(3)
C(7)	−545(4)	3 344(4)	2 203(3)
C(8)	−1 139(5)	4 054(5)	2 793(3)
C(9)	−429(5)	4 077(5)	3 498(3)
C(10)	858(5)	4 113(5)	3 388(3)
C(11)	1 321(4)	3 361(5)	2 794(3)
C(12)	732(4)	3 736(4)	2 080(3)
C(13)	825(5)	4 960(5)	1 869(3)
C(14)	23(7)	5 239(6)	1 228(4)
C(15)	770(5)	2 209(5)	2 897(3)
C(16)	−366(4)	2 146(4)	2 474(3)
O(1)	1 174(4)	1 462(4)	3 272(2)
O(2)	1 535(4)	4 708(4)	3 731(3)
Molecule 2			
C(1)	3 253(5)	1 349(5)	5 657(4)
C(2)	2 796(5)	1 030(6)	6 324(4)
C(3)	3 248(6)	121(6)	6 676(4)
C(4)	4 182(7)	−481(6)	6 422(4)
C(5)	4 666(6)	−180(5)	5 743(4)
C(6)	4 217(5)	749(5)	5 369(3)
C(7)	4 698(4)	1 057(5)	4 643(3)
C(8)	4 000(5)	491(5)	4 044(3)
C(9)	4 312(6)	845(6)	3 266(4)
C(10)	4 618(6)	2 070(6)	3 227(4)
C(11)	5 322(5)	2 538(5)	3 861(4)
C(12)	4 612(5)	2 339(5)	4 554(3)
C(13)	3 351(6)	2 745(6)	4 588(4)
C(14)	2 772(6)	2 366(6)	5 276(4)
C(15)	6 355(6)	1 735(6)	3 977(4)
C(16)	6 014(5)	854(5)	4 525(4)
O(1)	7 303(5)	1 824(4)	3 683(3)
O(2)	4 352(5)	2 653(5)	2 708(3)

n.m.r.). Saponification of the ester (4c) with 5% methanolic KOH afforded the acid (4b), m.p. and mixed m.p. 102 °C.

cis-3,4,4a,9,10,10a-*Hexahydro*-1,4a-*ethanophenanthrene*-2(1H),12-*dione* (5).—The *cis*-acetal aldehyde (3f) (0.8 g, 2.80 mmol) was warmed at 80 °C for 3 h with glacial acetic acid (22.5 ml) and water (2.5 ml) under an atmosphere of nitrogen and finally left overnight at room temperature. It was neutralised with solid Na_2CO_3, diluted with water, and extracted with ether. Removal of solvent gave a viscous liquid (0.65 g) [$\nu_{max.}$ 3 400 and 1 710 cm^{-1}], which was dissolved in acetone (15 ml) and treated with Jones reagent at 10—15 °C until the colour of the reagent persisted for 10 min. It was then stirred for a further 30 min. Excess of reagent was decomposed with propan-2-ol, diluted with water and extracted with ether. The ether extract was washed and dried (Na_2SO_4). Removal of solvent gave a colourless solid product (0.60 g, 89%), g.l.c. analysis of which showed it to be mixture of the diketone (5) and its C-3 epimer in the ratio 80—90 : 20—10. Recrystallisation twice from ethyl acetate–petroleum (1 : 1) gave the pure diketone (5) (0.45 g, 65%), m.p. 144 °C (Found: C, 80.2; H, 6.95. $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71%), $\nu_{max.}$ 1 745 and 1 705 cm^{-1}; δ(100 MHz), 1.70—3.16 (complex m, 11 H), 3.26 (d, 1 H, *J* 4 Hz, COCHCO),

Table 3. Bond distances (Å) and angles (°) of the asymmetric unit of the *cis*-diketone (5) (Figure 1) with their e.s.d.s

(a) Bond distances (Å)

Bond specification	Molecule no. 1	Molecule no. 2
C(1)–C(2)	1.391(8)	1.392(9)
C(1)–C(6)	1.403(8)	1.414(8)
C(1)–C(14)	1.513(9)	1.507(9)
C(2)–C(3)	1.370(9)	1.366(9)
C(3)–C(4)	1.389(9)	1.367(9)
C(4)–C(5)	1.399(9)	1.418(9)
C(5)–C(6)	1.393(7)	1.403(9)
C(6)–C(7)	1.529(7)	1.497(8)
C(7)–C(8)	1.538(7)	1.521(8)
C(7)–C(12)	1.545(7)	1.542(8)
C(7)–C(16)	1.529(7)	1.533(8)
C(8)–C(9)	1.534(8)	1.542(9)
C(9)–C(10)	1.480(8)	1.505(9)
C(10)–C(11)	1.515(8)	1.526(9)
C(11)–C(12)	1.548(8)	1.535(9)
C(11)–C(15)	1.523(8)	1.533(9)
C(12)–C(13)	1.517(8)	1.517(9)
C(13)–C(14)	1.534(9)	1.504(9)
C(15)–C(16)	1.513(8)	1.512(9)
C(15)–O(1)	1.220(7)	1.214(9)
C(10)–O(2)	1.224(7)	1.224(9)

(b) Bond angles (°)

Angle specification	Molecule no. 1	Molecule no. 2
C(2)–C(1)–C(6)	118.5(5)	119.0(6)
C(2)–C(1)–C(14)	118.0(5)	119.9(6)
C(6)–C(1)–C(14)	123.4(5)	120.9(6)
C(1)–C(2)–C(3)	121.0(6)	119.9(6)
C(2)–C(3)–C(4)	121.0(6)	123.2(7)
C(3)–C(4)–C(5)	118.9(6)	118.2(7)
C(4)–C(5)–C(6)	120.1(5)	119.7(6)
C(1)–C(6)–C(5)	120.4(5)	119.8(6)
C(1)–C(6)–C(7)	118.4(4)	119.8(6)
C(5)–C(6)–C(7)	121.2(5)	120.2(5)
C(6)–C(7)–C(8)	109.8(4)	110.7(5)
C(6)–C(7)–C(12)	107.6(4)	108.4(5)
C(6)–C(7)–C(16)	116.7(4)	116.5(5)
C(8)–C(7)–C(12)	110.6(4)	109.3(5)
C(8)–C(7)–C(16)	110.0(4)	109.6(5)
C(12)–C(7)–C(16)	101.9(4)	101.8(4)
C(7)–C(8)–C(9)	112.4(4)	116.0(5)
C(8)–C(9)–C(10)	114.0(5)	111.3(6)
C(9)–C(10)–C(11)	115.2(5)	116.1(6)
C(9)–C(10)–O(2)	124.6(5)	122.2(6)
C(11)–C(10)–O(2)	120.1(5)	121.6(6)
C(10)–C(11)–C(12)	107.3(4)	108.0(5)
C(10)–C(11)–C(15)	107.6(5)	106.4(5)
C(12)–C(11)–C(15)	100.9(4)	100.9(5)
C(7)–C(12)–C(11)	101.1(4)	102.1(5)
C(7)–C(12)–C(13)	113.3(4)	111.9(5)
C(11)–C(12)–C(13)	117.9(4)	118.9(5)
C(12)–C(13)–C(14)	111.5(5)	110.7(6)
C(1)–C(14)–C(13)	116.9(5)	118.6(6)
C(11)–C(15)–C(16)	109.4(5)	109.4(5)
C(11)–C(15)–O(1)	125.2(5)	124.3(6)
C(16)–C(15)–O(1)	125.4(5)	126.2(6)
C(7)–C(16)–C(15)	103.7(4)	103.7(5)

and 7.16br (s, 4 H, ArH); *m/z* 240 (M^+, 16%), 198 (17), 170 (13), 156 (74), 142 (43), 141 (100), 128 (82), and 115 (39).

trans-3,4,4a,9,10,10a-*Hexahydro*-3,4a-*ethanophenanthrene*-2(1H),12-*dione* (6).—The *trans*-acetal aldehyde (4f) (0.8 g, 2.80 mmol) was similarly subjected to intramolecular aldol condensation followed by a Jones oxidation as above to give

Table 4. Positional parameters ($\times 10^4$) of the non-hydrogen atoms of the molecule of the *trans*-diketone (6) (Figure 2) with their e.s.d.s

Atom	*x*	*y*	*z*
C(1)	2 761(5)	3 484(6)	−3 939(4)
C(2)	3 506(6)	5 188(7)	−4 064(5)
C(3)	3 683(7)	5 801(8)	−5 265(5)
C(4)	3 107(7)	4 706(9)	−6 366(5)
C(5)	2 409(6)	3 014(9)	−6 251(4)
C(6)	2 231(5)	2 369(7)	−5 047(4)
C(7)	1 497(6)	458(8)	−4 990(4)
C(8)	1 850(6)	−331(7)	−3 605(5)
C(9)	1 448(6)	1 197(7)	−2 707(4)
C(10)	1 383(6)	393(8)	−1 370(5)
C(11)	1 337(6)	1 872(9)	−370(5)
C(12)	2 371(6)	3 571(8)	−417(4)
C(13)	1 943(5)	4 400(7)	−1 819(4)
C(14)	2 600(5)	2 883(7)	−2 591(4)
C(15)	4 256(5)	2 455(7)	−1 666(4)
C(16)	4 041(6)	2 836(8)	−307(4)
O(1)	5 049(5)	2 615(6)	706(3)
O(2)	587(5)	1 708(7)	453(4)

the *trans*-diketone (6) (0.55 g, 81%) as the sole product (g.l.c.); m.p. 162 °C (ethyl acetate–petroleum) (Found: C, 79.8; H, 6.7 $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71%), $\nu_{max.}$ 1 750 and 1 705 cm^{-1}; δ (100 MHz) 1.56—3.14 (complex m, 11 H), 3.39 (d, 1 H, *J* 6 Hz, COCHCO), and 7.08—7.52 (m, 4 H, ArH); *m/z* 240 (M^+, 34%), 198 (61), 183 (9), 170 (11), 156 (100), 142 (27), 141 (52), 127 (93), and 115 (82).

Conversion of the cis-*Diketone* (5) *into the Keto-ester* (3a).—The *cis*-diketone (5) (100 mg, 0.42 mmol) was refluxed in benzene (10 ml) containing toluene-*p*-sulphonic acid (40 mg) and water (0.1 ml) for 4 h. The solution was then cooled and washed with 5% aqueous sodium hydrogencarbonate. Drying and evaporation of the solvent gave practically no residue. The hydrogencarbonate extract was next acidified and extracted with ether after saturation with sodium chloride. The ether extract was washed with brine, dried, and solvent removed to yield an acid which on treatment with ethereal diazomethane afforded the known keto-ester (3a) (100 mg, 88%) identical in all respects (i.r. and ^1H n.m.r.) with the sample described earlier.

Conversion of the trans *Diketone* (6) *into* 2′β-*Methoxycarbonyl*-1′,2′,3′,4′-*tetrahydrospiro*[*cyclopentane*-1,1′-*naphthalen*]-3′-*one*.—The *trans*-diketone (6) (100 mg, 0.42 mmol) was treated with toluene-*p*-sulphonic acid in wet benzene, as in case of the *cis*-diketone (5). A similar work-up afforded the acid (14) (90 mg, 83.7%), m.p. 136 °C (ether–light petroleum) (Found: C, 74.2; H, 7.05. $C_{16}H_{18}O_3$ requires C, 74.39; H, 7.02%), $\nu_{max.}$ 1 720 and 1 740 cm^{-1}.

The acid (14) on esterification with ethereal diazomethane afforded the corresponding methyl ester (15), $\nu_{max.}$ 1 735 cm^{-1}; δ 1.50—2.93 (m, 13 H), 3.50 (s, 3 H, CO_2CH_3), and 6.93—7.16 (m, 4 H, ArH).

Crystallographic Analysis of the cis-*Diketone* (5).—*Crystal data*. $C_{16}H_{16}O_2$, $M = 240$; Orthorhombic space group $Pca\,2_1$, $a = 11.385(9)$, $b = 11.938(8)$, $c = 18.50(2)$ Å, $Z = 8$, $D_c = 1.20$ g cm^{-3}, $F(000) = 1\,024$, μ(Cu-K_α) 5.22 cm^{-1}, 1 472 observed reflections with $|F| \geq 2\sigma(|F|)$ and $\theta \leq 55°$ were measured on a CAD-4 diffractometer. The structure was solved by MULTAN-78 [33] using the known orientation of one molecule of the asymmetric unit obtained from a previous MULTAN run and refined by the full-matrix least-square method to *R* 0.047. A view of the asymmetric unit of (5) along the *b* axis is shown in Figure 1. Positional parameters are given in Table 2 and bond distances and bond angles in Table 3.

Table 5. Bond distances (Å) and angles (°) of the molecule of the *trans*-diketone (6) with their e.s.d.s

(a) Bond distances

Bond specification	Distance	Bond specification	Distance
C(1)–C(2)	1.401(7)	C(9)–C(14)	1.551(7)
C(1)–C(6)	1.398(6)	C(10)–C(11)	1.502(8)
C(1)–C(14)	1.525(6)	C(11)–C(12)	1.517(8)
C(2)–C(3)	1.384(7)	C(11)–O(2)	1.209(6)
C(3)–C(4)	1.390(8)	C(12)–C(13)	1.553(6)
C(4)–C(5)	1.371(9)	C(12)–C(16)	1.514(7)
C(5)–C(6)	1.395(6)	C(13)–C(14)	1.546(6)
C(6)–C(7)	1.516(8)	C(14)–C(15)	1.553(6)
C(7)–C(8)	1.526(7)	C(15)–C(16)	1.515(6)
C(8)–C(9)	1.542(7)	C(16)–O(1)	1.214(6)
C(9)–C(10)	1.538(7)		

(b) Bond angles

Angle specification	Angle	Angle specification	Angle
C(2)–C(1)–C(6)	118.8(4)	C(10)–C(11)–O(2)	123.2(5)
C(2)–C(1)–C(14)	118.8(4)	C(12)–C(11)–O(2)	121.6(5)
C(6)–C(1)–C(14)	122.3(4)	C(11)–C(12)–C(13)	109.4(4)
C(1)–C(2)–C(3)	121.2(5)	C(11)–C(12)–C(16)	106.0(4)
C(2)–C(3)–C(4)	119.3(5)	C(13)–C(12)–C(16)	102.0(4)
C(3)–C(4)–C(5)	120.0(6)	C(12)–C(13)–C(14)	101.6(4)
C(4)–C(5)–C(6)	121.4(5)	C(1)–C(14)–C(9)	110.4(4)
C(1)–C(6)–C(5)	119.1(4)	C(1)–C(14)–C(13)	115.0(4)
C(1)–C(6)–C(7)	122.5(4)	C(1)–C(14)–C(15)	111.3(4)
C(5)–C(6)–C(7)	118.4(4)	C(9)–C(14)–C(13)	106.1(4)
C(6)–C(7)–C(8)	112.6(4)	C(9)–C(14)–C(15)	111.8(4)
C(7)–C(8)–C(9)	107.7(4)	C(13)–C(14)–C(15)	102.0(4)
C(8)–C(9)–C(14)	111.4(4)	C(14)–C(15)–C(16)	104.7(4)
C(10)–C(9)–C(14)	112.6(4)	C(12)–C(16)–C(15)	108.9(4)
C(9)–C(10)–C(11)	113.2(4)	C(12)–C(16)–O(1)	125.4(5)
C(10)–C(11)–C(12)	115.2(5)	C(15)–C(16)–O(1)	125.7(5)

The thermal parameters and the structure factors for compounds (5) and (6) are given in a Supplementary publication [SUP No. 23708 (23 pp.)].*

Crystallographic Analysis of the trans-*Diketone* (6).—*Crystal data*. $C_{16}H_{16}O_2$, $M = 240$; Monoclinic space group $P2_1$, $a = 8.638(1)$, $b = 7.160(1)$, $c = 10.554(1)$ Å, $\beta = 104.08(1)°$, $Z = 2$, $D_c = 1.26$ g cm^{-3}, $F(000) = 256$, μ(Mo-K_α) = 0.88 cm^{-1}, 1 080 observed reflections with $|F| \geq 2\sigma(|F|)$ and $\theta \leq 30°$ were measured on a CAD-4 diffractometer. The structure was solved by MULTAN-78 [33] and refined by the full-matrix least-squares method to *R* 0.047. The view of the asymmetric unit of (6) along the *b* axis is shown in Figure 2. Positional parameters are given in Table 4 and bond distances and bond angles in Table 5.

Acknowledgements

The financial support from Science and Engineering Research Council/D.S.T. Scheme under Grant No. 23 (3p-8)/81-STP/II is gratefully acknowledged. A.K.C. thanks Dr. S. C. Pakrashi for his encouragement.

* For details of the Supplementary Publications scheme, see Instructions for Authors (1983), *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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Received 14*th March* 1983; *Paper* 3/388