Condensed Cyclic and Bridged-ring Systems. Part 10.[1] Alumina-induced Regioselective Intramolecular Alkylations of *cis*- and *trans*-4a-(2-Methylsulphonyloxyethyl)-3,4,4a,9,10,10a-hexahydrophenanthren-2(1H)-ones

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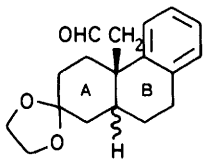
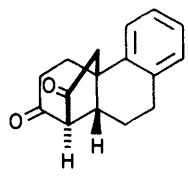
The synthesis and intramolecular alkylations of *cis*- and *trans*-4a-(2-methylsulphonyloxyethyl)-3,4,4a,9,10,10a-hexahydrophenanthren-2(1H)-ones (**5a**) and (**6a**), and the respective 6- and 5-methoxy analogues (**5b**) and (**5c**), and (**6b**) and (**6c**), are described. While alumina-induced alkylation of the *cis*-isomers (**5a**) and (**5b**) is shown to give, in each case, a mixture of the corresponding regioisomeric bridged-ketones, *cis*-3,4,4a,9,10,10a-hexahydro-1,4a-ethanophenanthren-2(1*H*)-one (**23a**) and *cis*-3,4,4a,9,10,10a-hexahydro-3,4a-ethanophenanthren-2(1*H*)-one (**24a**), and the 6-methoxy derivatives (**23b**) and (**24b**) in a ratio of *ca.* 3—4:1, the *trans*-isomers (**6a—c**) produce exclusively the respective *trans*-hexahydro-3,4a-ethanophenanthren-2(1*H*)-ones (**26a—c**). Alkylation of the *cis*-ketone (**5a**) with sodium hydride in benzene gives a 3:1 mixture of isomers (**23a**) and (**24a**), whereas with potassium t-butoxide in t-butyl alcohol the only isolable product is *cis*-3-hydroxy-4a,9,10,10a-tetrahydro-1,4a-ethanophenanthren-2(1*H*)-one (**25**) [arising from the concomitant autoxidation of the major alkylated product (**23a**)]. Using sodium hydride or potassium t-butoxide as the base, the *trans*-ketone (**6a**) gives *trans*-3,4,4a,9,10,10a-hexahydro-3,4a-ethanophenanthren-2(1*H*)-one (**26a**) as the sole product. The attempted preparation of the 5-methoxy-methanesulphonate (**5c**) from the corresponding *cis*-keto-alcohol (**21c**) led to *cis*-3,4,4a,9,10,10a-hexahydro-5,4a-(epoxyethano)phenanthren-2(1*H*)-one (**27**) *via* elimination of the aromatic methoxy methyl group.

In the preceding paper in this series[1] we reported that the epimeric *cis*- and *trans*-octahydrophenanthrene acetal aldehydes (**1**) and (**2**) give the isomeric bridged diketones (**3**) and (**4**), respectively, in good yields, by acid-catalysed deacetalation with concomitant, highly regioselective intramolecular aldol condensation, followed by Jones oxidation of the intermediate bridged ketols. In connection with the synthesis of some complex diterpenoids and related compounds,[2] we set out to determine whether the intramolecular C-alkylation of the epimeric keto-methanesulphonates, for example (**5a**) and (**6a**), would show the same regioselectivity as that of the aldol condensations in the bridged ring formation. Although base-catalysed intramolecular alkylations of polycyclic ketones have been extensively investigated,[3] the influence of the ring-junction stereochemistry on the regioselectivity in such reactions has not been evaluated. In this paper we describe the preparation and intramolecular alkylations of the epimeric keto-methanesulphonates (**5a—c**) and (**6a—c**); we have found that alumina is a highly efficient catalyst in these carbon–carbon bond formation reactions.



(1) A/B – *cis*
(2) A/B – *trans*



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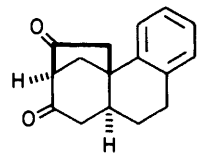


(4)

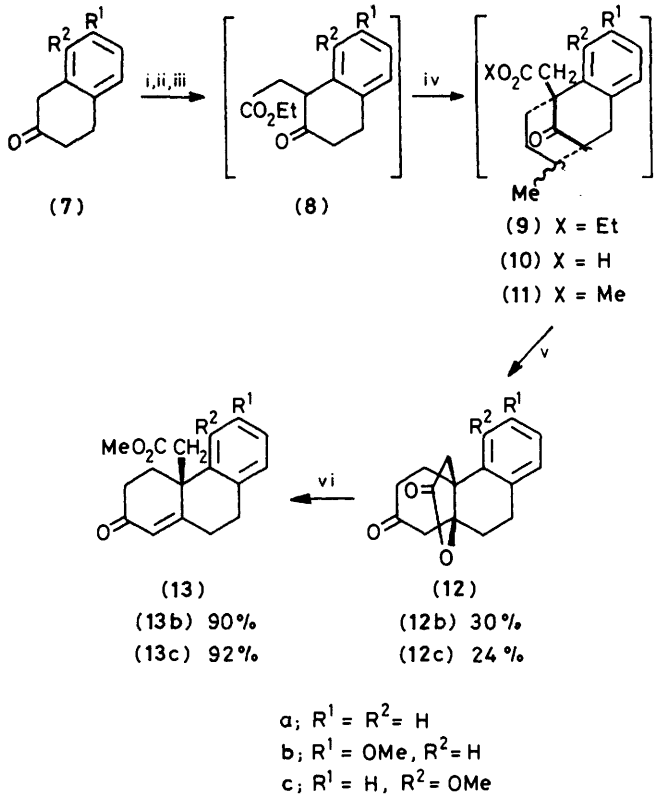
(5)

(6)

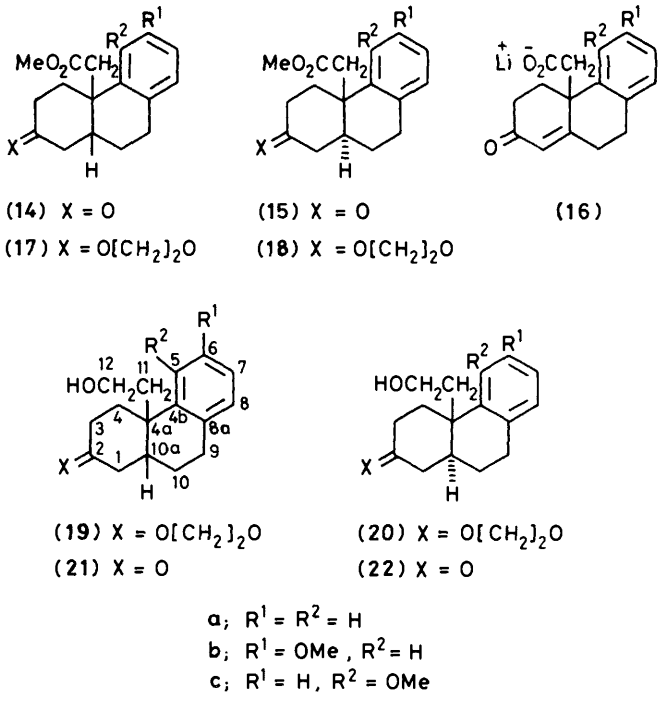
a; $R^1 = R^2 = H$
b; $R^1 = OMe$, $R^2 = H$
c; $R^1 = H$, $R^2 = OMe$

Results and Discussion

Synthesis of the Starting Methanesulphonates.—Our previously reported [1] acetal alcohols (**19a**) and (**20a**) served as the starting materials for the keto-alcohols (**21a**) and (**22a**), precursors for the methanesulphonates (**5a**) and (**6a**). For the synthesis of the methoxy analogues, through a similar sequence, we required the corresponding key intermediate keto-lactones (**12b**) and (**12c**) and the keto-esters (**13b**) and (**13c**). These were prepared from the respective dihydronaphthalen-2(1*H*)-ones (**7b**)[4] and (**7c**)[5] through the ketoesters (**8b**) and (**8c**) by using the method of Evans *et al.*[6] for the demethoxy analogues (**12a**) and (**13a**) (Scheme). It should be noted that in the latter case, in addition to the keto-lactone (**12c**) (24%), a solid acidic product



Scheme. *Reagents:* i, pyrrolidine, benzene; ii, $BrCH_2CO_2Et$, benzene; iii, HCl, H_2O; iv, $MeCOCH{=}CH_2$, MeOH, H_2O, KOH; v, heat, HCl, H_2O; vi, K_2CO_3, MeI, acetone



(*ca.* 8%), assigned as the epimeric ketol acids* (**10c**), was also isolated. The structures of (**10c**) were assigned from the spectral data of the corresponding methyl esters (**11c**) (see Experimental section). Finally, treatment of compounds (**12b**) and (**12c**) with potassium carbonate and methyl iodide produced the respective keto-esters (**13b**) and (**13c**) in excellent yield.

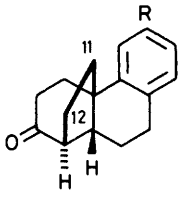
As observed[1] for the demethoxy analogue (**13a**), the catalytic hydrogenation of compounds (**13b**) and (**13c**) in pyridine[7] over palladium–charcoal (10%) proceeded with a high degree of stereoselectivity, leading almost exclusively to the pure *cis*-epimers (**14b**) and (**14c**), respectively. Repeating the hydrogenation of (**13b**) in *N,N*-dimethylformamide[8] (DMF) produced a mixture of (**14b**) and the *trans*-epimer (**15b**) in the ratio 2:1 whereas (**13c**) gave the respective *cis*- and *trans*-epimers (**14c**) and (**15c**) in the ratio 14:86, from which (**15c**) could be easily separated. As reported previously,[1] the analogous reduction of (**13a**) gave a 2:3 mixture of the corresponding *cis*- and the *trans*-epimers (**14a**) and (**15a**). Thus, it appears that the nature of the aromatic substituent has a profound influence on the stereochemical outcome in the catalytic hydrogenation of (**13a**—**c**) in DMF.

In accord with our previous finding[1] with (**16a**), the lithium–ammonia reduction of the lithium salt (**16b**), prepared from the respective keto-lactone (**12b**), with lithium methoxide followed by esterification (diazomethane) of the resulting acidic product and Jones oxidation gave a practically pure sample of the *trans*-epimer (**15b**) (58%). The similar reduction of (**16c**) proceeded with a somewhat decreased stereoselectivity, leading to a mixture of the *cis*- and *trans*-keto-esters (**14c**) and (**15c**) in the ratio 18:82. Each of the epimeric keto-esters (**14b**), (**14c**), (**15b**), and (**15c**) was transformed into the respective acetal esters (**17b**), (**17c**), (**18b**), and (**18c**), by a standard procedure;[1] these, on reduction with lithium aluminium hydride, afforded the corresponding acetal alcohols (**19b**), (**19c**), (**20b**), and (**20c**), in excellent overall yields. These and the previously described demethoxy analogues[1] (**19a**) and (**20a**), on deacetalation with aqueous methanolic hydrochloric acid, gave the respective keto-alcohols (**21a**—**c**) and (**22a**—**c**). The crystalline methanesulphonates (**5a**) and (**6a**) were obtained in good yields, by treatment of (**21a**) and (**22a**) with methanesulphonyl chloride and pyridine in dichloromethane.[3a] The crude methanesulphonates (**5b**), (**6b**), and (**6c**), prepared by an identical method, were used directly for the subsequent alkylation reactions. However, the attempted transformation of (**21c**) into (**5c**) (described later) gave an entirely different course of reaction.

The stereochemistries assigned to the aforementioned new methoxyoctahydrophenanthrene derivatives are based upon the following ^{13}C n.m.r. spectral data. As reported in our earlier paper,[1] the C-11 signal of *cis*-4a-substituted octahydrophenanthrene derivatives [*e.g.* (**14a**) and (**19a**)] is characteristically shifted significantly downfield relative to that of the *trans*-epimers (**15a**) and (**20a**). Thus, in the *cis*-6-methoxy derivatives (**14b**), (**19b**), and (**21b**), the C-11 signal occurs *ca.* 0—12 p.p.m. downfield of that of the respective *trans*-epimers (**15b**), (**20b**), and (**22b**). In the 5-methoxy series, however, the difference between the C-11 chemical shifts of the *cis*-epimers (**14c**), (**19c**), and (**21c**) and those of the *trans*-epimers (**15c**), (**20c**), and (**22c**) is *ca.* 5—7 p.p.m. (see Experimental section); this smaller degree of deshielding in the 5-methoxyoctahydrophenanthrene derivatives may be attributed to 'steric compression'[9] between C-11 and the OMe group.

Intramolecular Alkylation Reactions.—The first compounds to be studied in detail were the simple epimeric *cis*- and *trans*-methanesulphonates (**5a**) and (**6a**). Thus, treatment of compound (**5a**) with sodium hydride in benzene under reflux afforded a mixture of the regioisomeric bridged ketones (**23a**)

* Although the intermediate epimeric ketol esters (**9a**) in the corresponding annelation of the keto-ester (**7a**) have been well characterised,[6] the isolation of the corresponding acids (**10a**) has not been reported.



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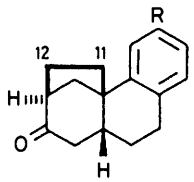
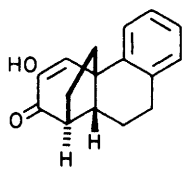


(24)

a; R = H
b; R = OMe



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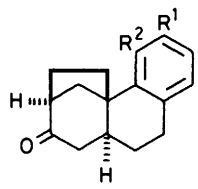

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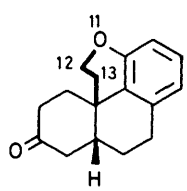

(27)

a; $R^1 = R^2 = H$
b; R^1 = OMe, R^2 = H
c; R^1 = H, R^2 = OMe

and (**24a**) (57%) in the ratio *ca.* 3:1 (g.l.c.). This mixture showed a cyclohexanone C=O band at 1 710 cm^{-1} and gave the correct elemental analyses. In the ^{13}C n.m.r. spectrum, the major isomer exhibited deshielding (*ca.* 10 p.p.m.) of the C-1 and C-10a signals with respect to that of the keto-alcohol (**21a**); it was therefore assigned structure (**23a**), resulting from alkylation at C-1 in (**5a**). The weak signals at 46.9 and 52.2 p.p.m. are possibly due to C-4 and C-3 of the minor isomer (**24a**) (see Experimental section).

Repeating the alkylation of compound (**5a**), with potassium t-butoxide in t-butyl alcohol at room temperature under nitrogen (without any special precaution to exclude traces of oxygen) gave a crystalline enolised α-diketone (**25**) (48%) as the only isolable product, after chromatography on silica gel. The same product was also obtained, in poor yield, when the aforementioned 3:1 mixture of (**23a**) and (**24a**) was treated similarly. The trace of oxygen contaminating the nitrogen is possibly responsible for the facile oxidation of the major ketone (**23a**) into compound (**25**), presumably by way of an intermediate hydroperoxy-ketone; such intermediates are known[10] to be readily generated in potassium t-butoxide in butanol. The structure of compound (**25**), initially assigned from the spectral and analytical data (see Experimental section) has been confirmed by an *X*-ray crystal structure analysis at the *X*-ray laboratory of the Presidency College, Calcutta, by Pal *et al.**

In contrast to the *cis*-epimer (**5a**), the *trans*-methanesulphonate (**6a**) gave the crystalline bridged ketone (**26a**) (58—61%) as the sole alkylation product, both with sodium hydride in benzene or potassium t-butoxide in t-butyl alcohol. The deshielding of the signals due to C-3 and C-4 by *ca.* 13 and 11 p.p.m. respectively in (**26a**), with respect to that of the keto-alcohol (**22a**), in the ^{13}C n.m.r. spectra clearly demonstrates that this product must arise from alkylation at C-3 in compound (**6a**).

We also examined a number of other alkylation conditions with compounds (**5a**) and (**6a**), using different combinations of base and solvents, but none of those appeared sufficiently promising to warrant discussion. The remarkably mild conditions which finally resulted from the work show that ordinary chromatographic alumina is an excellent catalyst[11] for the intramolecular alkylations† of the keto-methanesulphonates (**5a**), (**5b**), and (**6a—c**).

Thus, treatment of the *cis*-methanesulphonate (**5a**) in dichloromethane with neutral alumina at room temperature for three days, led to the complete disappearance of the starting material (^1H n.m.r.) and afforded a 3:1 mixture of products (**23a**) and (**24a**). Similarly, the crude methanesulphonate (**5b**), prepared from the 6-methoxy-2-oxo-alcohol (**21b**), gave a 4:1 mixture of (**23b**) and (**24b**) (g.l.c.). The spectral and analytical data for this mixture (see Experimental section) are consistent with the assigned structures.

The *trans*-keto-methanesulphonates (**6a—c**), on alumina-catalysed alkylation, gave the respective crystalline bridged ketones (**26a—c**) in good yields. In the case of the *trans*-methanesulphonates the reactions were virtually completed within 24 h. The stereoelectronically favourable relationships between the leaving methanesulphonate group and the alumina-generated enolate ion in the *trans*-epimers is possibly responsible for their facile alkylation reactions.

As mentioned above, interaction of the 5-methoxy substituted *cis*-keto-alcohol (**21c**) with methanesulphonyl chloride in the presence of pyridine gave a mixture of products, consisting of the cyclic keto-ether (**27**) with only a trace of the expected methanesulphonate (**5c**) (^1H n.m.r.). The crude mixture, on treatment with alumina, gave crystalline (**27**) (40%). The structure of compound (**27**) has been assigned from the spectral data and the elemental analyses.

The facile formation of the epoxyethano bridged compound (**27**) can be attributed to the proximity of the OMe group to the leaving methanesulphonate group in the intermediate (**5c**) enabling the formation of an oxonium ion; this is then attacked by an anion at the least hindered methyl residue to give the cyclic keto-ether with the elimination of the methyl group, as observed recently[14] in the case of some triptycene systems.

The present results clearly indicate that, irrespective of the reaction conditions, intramolecular alkylations of the epimeric *cis*- and *trans*-keto-methanesulphonates (**5a**) and (**5b**), and (**6a—c**), proceed preferentially by enolization of C-1 and C-3, respectively; this is analogous to the aldol condensations[1] of the enolates generated from the *cis*- and *trans*-acetal aldehydes, (**1a**) and (**2a**), and parallels the regiochemistry of enolization in the A/B-*cis*- and -*trans*-3-oxo-steroids.[1] Perhaps the most significant outcome of the present work is the demonstration of the high efficiency of alumina in the intramolecular alkylation reactions.

Experimental

The compounds described are all racemates. M.p.s and b.p.s are not corrected. I.r. spectra were recorded on a Perkin-Elmer model PE 298 spectrometer. U.v. spectra were recorded on a Beckman DU spectrometer for solutions in 95% ethanol. ^1H N.m.r. spectra were taken at 60 MHz on a Varian T-60A spectrometer, with $SiMe_4$ as internal standard. ^1H N.m.r. (at 100 MHz) and ^{13}C n.m.r. spectra were recorded on a Jeol FX-100 Fourier transform n.m.r. spectrometer. Mass spectra were obtained using a Hitachi RMU-6 instrument. Analytical g.l.c. was performed on a Hewlett-Packard 5730A chromatograph equipped with a flame-ionization detector [6 ft × 1/8 in 3% SE-52 (Column A) or 20 × 1/8 in 10% UCW (Column B)] with N_2

* A. K. Pal, B. N. Das, and B. S. Basak, manuscript in preparation. We thank Professor Basak and Dr. Das for forwarding us the perspective drawing of the final *X*-ray model of (**25**).

† Two examples of alumina-promoted intramolecular substitution by nucleophilic carbon atoms, leading to cyclopropane ring formation, have been reported.[12,13]

as the carrier gas. Elemental analyses were performed by Mr. P. P. Bhattacharyya of this laboratory. Column chromatography and alkylation reactions were performed on neutral alumina (Brockman Grade I). Petroleum and light petroleum refer to the fractions with b.p.s 60—80 and 40—60 °C respectively. Ether refers to diethyl ether.

10a-*Hydroxy*-6-*methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetic Acid* 4a,10a-*Lactone* (**12b**).—The procedure described by Evans *et al.*[6] for the preparation of the respective demethoxy analogue (**12a**) was adopted. The crude enamine, prepared from the dihydronaphthalenone (**7b**)[4] (22 g, 0.13 mol) and freshly distilled pyrrolidine (30 ml) in benzene (300 ml), was alkylated by reflux with ethyl bromoacetate (34.5 g, 0.21 mol) in dry benzene (140 ml) for 4 h under N_2. The benzene was distilled off and the immonium salt was hydrolysed by reflux for 1 h with methanol (130 ml) and water (100 ml). The reaction mixture was cooled, diluted with 10% HCl (150 ml), and extracted repeatedly with benzene. The organic layer was washed with water until neutral and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded a pale yellow oil, which was distilled to give ethyl 7-methoxy-2-oxo-1,2,3,4-tetrahydronaphthalen-1-ylacetate (**8b**) (22.1 g), b.p. 165—170 °C (0.2 mmHg); $\nu_{max.}$($CHCl_3$) 1 720 and 1 735 cm^{-1}; δ(CCl_4) 1.20 and 4.08 (t, q, *J* 7 Hz, CH_3CH_2O), 3.70 (s, OMe), and 3.80 (t, methine H). The ^1H n.m.r. spectrum indicated the presence of a small amount of unchanged (**7b**).

To a well stirred solution of compound (**8b**) (21 g, 0.08 mol) in methanol (150 ml), cooled in an ice–salt bath (*ca.* −10 °C) under N_2, a precooled solution of KOH (10 g, 0.18 mol) in water (13.5 ml) and methanol (27 ml) was added in one portion with stirring. To this, a solution of freshly distilled methyl vinyl ketone (7.65 g, 0.13 mol) in methanol (15 ml) was added dropwise during 1 h at −10 °C. The mixture was stirred at the same temperature for another 2 h, left overnight at room temperature, and then refluxed for 2 h, cooled in an ice-bath, and acidified to pH 3—5 with 12M-HCl. It was then diluted with water (600 ml) and extracted with chloroform and the organic layer washed with water, dried (Na_2SO_4), and evaporated. After trituration of the crude crystalline material with ether (50 ml), the *keto-lactone* (**12b**) (10.5 g 30% overall yield) was obtained, m.p. 182 °C (acetone–petroleum) (Found: C, 71.3; H, 6.2. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.35%); $\nu_{max.}$(KBr) 3 060, 3 000, 2 940, 2 920, 2 860, 1 765, 1 710, 1 610, 1 505, 1 440, 1 420, 1 315, 1 300, 1 240, 1 180, 1 120, 1 030, 1 005, 980, 940, 920, 870, 820, 800, 755, and 720 cm^{-1}; δ_H($CDCl_3$) 1.67—2.93 (12 H, m), 3.80 (3 H, s, ArOMe), and 6.63—7.30 (3 H, m, ArH); δ_C($CDCl_3$) 207.8 (s, C-2), 174.1 (s, C-12), 158.8 (s, C-6), 140.0 (s, C-4b), 129.9 (d, C-8), 126.3 (s, C-8a), 112.5 and 112.2 (d, C-5 and C-7), 87.1 (s, C-10a), 55.2 (q, ArOMe), 48.0 (t, C-1), 44.0 (t and s, C-11 and C-4a), 35.5 (t, C-3), 34.1 (t, C-4), 33.8 (t, C-10), and 25.4 p.p.m. (t, C-9).

10a-*Hydroxy*-5-*methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetic Acid* 4a,10a-*Lactone* (**12c**) *and the Epimeric Bridged Ketol Acids* (**10c**).—The crude pyrrolidine enamine from the dihydronaphthalenone (**7c**)[5] (22 g, 0.13 mol) was alkylated with ethyl bromoacetate (34.5 g, 0.21 mol) as described above to afford ethyl 8-methoxy-2-oxo-1,2,3,4-tetrahydronaphthalene-1-ylacetate (**8c**) (22.2 g), b.p. 165—170 °C (0.25 mmHg); $\nu_{max.}$($CHCl_3$) 1 720 and 1 735 cm^{-1}; δ(CCl_4) 1.13 and 3.90 (t, q, *J* 7 Hz, CH_3CH_2O) and 3.40 (s, OMe). The methine proton was overlapped with the OMe signal of a small amount of unchanged (**7c**).

The keto-ester (**8c**) (21 g, 0.08 mol) was condensed with methyl vinyl ketone (7.65 g, 0.13 mol) in the presence of KOH (10 g, 0.18 mol) in aqueous methanol as described above. During extraction with chloroform, an insoluble solid material formed and this was filtered off; the filtrate was washed with water, dried, and evaporated. The residue, on trituration with ether, solidified to afford the *keto-lactone* (**12c**) (8.5 g, 24% overall yield), m.p. 202 °C (acetone) (Found: C, 71.45; H, 6.55. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.35%); $\nu_{max.}$(KBr) 3 080, 3 000, 2 940, 2 865, 1 780, 1 720, 1 600, 1 580, 1 470, 1 270, 1 260, 1 225, 1 190, 1 085, 1 020, 975, 875, 790, and 750 cm^{-1}; δ_H($CDCl_3$) 1.73—3.16 (12 H, m), 3.86 (3 H, s, ArOMe), and 6.63—7.40 (3 H, m, ArH); δ_C($CDCl_3$) 208.4 (s, C-2), 175.1 (s, C-12), 157.8 (s, C-5), 136.3 (s, C-8a), 127.9 (d, C-7), 121.5 (d, C-8), 109.6 (d, C-4b and C-6), 87.4 (s, C-10a), 55.3 (q, ArOMe), 48.6 (t, C-1), 43.3 (s, C-4a), 42.1 (t, C-11), 35.9 (t, C-3), 34.1 (t, C-10), 30.7 (t, C-4), and 26.9 p.p.m. (t, C-9).

The aqueous layer, after extraction with chloroform, was saturated with NaCl and re-extracted with ethyl acetate. The ethyl acetate extracts were combined with a solution of the aforementioned chloroform-insoluble material in the same solvent. The combined ethyl acetate layer was washed with brine and dried and the solvent removed to yield the epimeric 9-*hydroxy*-8-*methoxy*-9-*methyl*-1,2,3,4-*tetrahydro*-1,3-*propanonaphthalen*-1-*ylacetic acids* (**10c**) (3 g, 8% overall yield), m.p. 222—226 °C (decomp.) (ethyl acetate–acetone) (Found: C, 67.0; H, 6.7. $C_{17}H_{20}O_5$ requires C, 67.1; H, 6.6%); $\nu_{max.}$(KBr) 3 520, 2 960, 2 860, 1 715, 1 705, 1 580, 1 470, 1 440, 1 350, 1 250, 1 225, 1 080, 920, 860, 850, 800, 780, and 740 cm^{-1}. The mixture of epimers of (**10c**) was esterified with an excess of diazomethane in ether to afford the corresponding methyl esters (**11c**) as a thick colourless liquid; $\nu_{max.}$(neat) 3 400, 2 960, 2 940, 2 820, 1 735, 1 705, 1 580, 1 470, 1 440, 1 400, 1 370, 1 360, 1 250, 1 200, 1 160, 1 080, 1 005, 990, 920, 795, and 775 cm^{-1}; δ_H($CDCl_3$) 1.23 and 1.30 (ratio 2:3, 2 s, epimeric C-CH_3), 1.60—3.40 [m, including a broad (OH) signal at 2.03 (exchangeable with D_2O)], 3.46 and 3.50 (2 s, epimeric CO_2Me), 3.76 (s, ArOMe), and 6.50—7.26 (m, ArH).

Methyl 6-*Methoxy*-2-*oxo*-2,3,4,4a,9,10-*hexahydrophenanthren*-4a-*ylacetate* (**13b**).—A solution of the keto-lactone (**12b**) (9 g, 31.5 mmol) in anhydrous acetone (200 ml) was refluxed on a steam-bath, with stirring, for 1 h under N_2 with anhydrous K_2CO_3 (10.5 g). To the cooled, stirred reaction mixture, MeI (9 ml) was added and refluxing continued for 2 h. An additional amount of MeI (9 ml) was then added and the mixture stirred and heated for 2 h. The acetone was removed under reduced pressure and the concentrate was diluted with benzene (500 ml) and water (250 ml). The benzene layer was separated, washed with water, 10% sodium thiosulphate solution, and water, dried (Na_2SO_4), and evaporated to afford the unsaturated *keto-ester* (**13b**) as a yellow solid (8.5 g, 90%), m.p. 98 °C (acetone–petroleum) (Found: C, 71.95; H, 6.75. $C_{18}H_{20}O_4$ requires C, 72.0; H, 6.7%); $\lambda_{max.}$ 230 and 282 nm (log ε 4.39, 3.60); $\nu_{max.}$(KBr) 3 100, 3 000, 2 920, 2 860, 2 840, 1 720, 1 665, 1 630, 1 605, 1 580, 1 500, 1 440, 1 425, 1 360, 1 320, 1 240, 1 205, 1 110, 1 040, 1 030, 1 005, 930, 870, 820, 775, 760, and 720 cm^{-1}; δ_H($CDCl_3$) 1.83—3.13 (10 H, m), 3.55 (3 H, s, CO_2Me), 3.76 (3 H, s, ArOMe), 5.96 (1 H, s, =CHCO), and 6.60—7.26 (3 H, m, ArH); δ_C($CDCl_3$) 197.6 (s, C-2), 170.3 (s, C-12), 166.4 (s, C-6), 158.0 (s, C-10a), 141.3 (s, C-4b), 129.2 (d, C-8), 126.8 (s, C-8a), 125.2 (d, C-1), 112.1 and 111.3 (d, C-5 and C-7), 54.8 (q, ArOMe), 51.2 (q, Me ester), 43.7 (t, C-11), 41.0 (s, C-4a), 34.5 and 34.1 (t, C-3 and C-4), 30.9 (t, C-10), and 29.3 p.p.m. (t, C-9).

Methyl 5-*Methoxy*-2-*oxo*-2,3,4,4a,9,10-*hexahydrophenanthren*-4a-*ylacetate* (**13c**).—The keto-lactone (**12c**) (9 g, 31.5 mmol) was treated with anhydrous K_2CO_3 (10.5 g) and MeI (18 ml) in dry acetone (200 ml) in a manner similar to that used for (**13b**) to afford the unsaturated *keto-ester* (**13c**) (8.7 g, 92%) as a pale yellow solid, m.p. 112 °C (acetone–petroleum) (Found: C, 71.8; H, 6.7. $C_{18}H_{20}O_4$ requires C, 72.0; H, 6.7%); $\lambda_{max.}$ 230 and 282 nm (log ε 4.41 and 3.43); $\nu_{max.}$(KBr) 3 100, 3 000, 2 960,

2 925, 2 820, 1 725, 1 665, 1 610, 1 600, 1 580, 1 470, 1 440, 1 415, 1 360, 1 340, 1 320, 1 260, 1 220, 1 200, 1 150, 1 090, 1 000, 945, 935, 880, 805, 790, 750, and 710 cm^{-1}; $\delta_H(CDCl_3)$ 1.67—3.33 (10 H, m), 3.49 (3 H, s, CO_2Me), 3.83 (3 H, s, ArOMe), 5.90 (1 H, s, =CHCO), and 6.60—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 198.4 (s, C-2), 171.5 (s, C-12), 169.3 (s, C-5), 157.9 (s, C-10a), 137.0 (s, C-8a), 128.3 (s, C-4b), 127.2 (d, C-7), 124.2 (d, C-1), 121.4 (d, C-8), 109.6 (d, C-6), 54.9 (q, ArOMe), 51.1 (q, Me ester), 42.7 (t, C-11), 41.6 (s, C-4a), 34.3, 34.0 (t, C-3 and C-4), 32.0 (t, C-10), and 31.5 p.p.m. (t, C-9).

cis-*Methyl* 6-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (**14b**).—The unsaturated keto-ester (**13b**) (3 g, 10 mmol) was hydrogenated in dry pyridine (60 ml) in the presence of 10% Pd–C (180 mg) at room temperature and pressure. After a theoretical quantity of hydrogen had been consumed, the catalyst was filtered off and the filtrate was diluted with ice-cold 2M-HCl (400 ml) and extracted with ether. The combined ethereal extracts were washed with water and dried (Na_2SO_4). Evaporation of the solvent afforded the cis-*keto-ester* (**14b**) (3 g, 99%) as a yellow oil, shown to be homogeneous by g.l.c. and ^1H n.m.r. An analytical sample was prepared by evaporative distillation at 180—185 °C (bath temp.) (0.08 mmHg), homogeneous on g.l.c. on column A (R_t 25 min) at 220 °C (Found: C, 71.4; H, 7.35. $C_{18}H_{22}O_4$ requires C, 71.5; H, 7.35%); $\nu_{max.}$(neat) 2 940, 2 820, 1 715, 1 600, 1 500, 1 250, 1 170, and 1 050 cm^{-1}; $\delta_H(CDCl_3)$ 1.67—3.00 (13 H, m), 3.58 (3 H, s, CO_2Me), 3.76 (3 H, s, ArOMe), and 6.60—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 210.5 (s, C-2), 170.7 (s, C-12), 157.8 (s, C-6), 139.6 (s, C-4b), 130.4 (d, C-8), 127.0 (s, C-8a), 111.9, 111.0 (d, C-5 and C-7), 54.8 (q, ArOMe), 51.0 (q, Me ester), 45.4 (t, C-11), 42.7 (t, C-1), 39.5 (s, C-4a), 38.2 (s, C-10a), 37.5 (t, C-3), 34.2 (t, C-4), 24.2 (t, C-9), and 23.5 p.p.m. (t, C-10).

trans-*Methyl* 6-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (**15b**).—The keto-lactone (**12b**) (1.3 g, 4.5 mmol) was converted into the lithium salt (**16b**) by heating under reflux for 4 h in methanol (100 ml) under N_2, with an excess of LiOMe, prepared from LiH (101 mg, 13.5 mmol) and methanol. The dried crude lithium salt was added to a well stirred mixture of anhydrous liquid NH_3 (200 ml) and tetrahydrofuran (THF) (20 ml) followed by small pieces of Li (190 mg, 27 mmol) during 5 min. The excess of solid NH_4Cl was added slowly and the ammonia was allowed to evaporate. After removal of the THF under reduced pressure the residue was acidified with an excess of 6M-HCl and extracted with ethyl acetate, dried (Na_2SO_4), and evaporated. The crude acidic product was esterified with an excess of ethereal diazomethane and showed a strong OH band in its i.r. spectrum. The product was dissolved in acetone and oxidized with Jones' reagent at 10—15 °C, until the colour of the reagent persisted for 10 min; it was then worked up in the usual way. The crude product was chromatographed on neutral alumina. Elution with benzene–petroleum (3:1 v/v) afforded the trans-*keto-ester* (**15b**) (800 mg, 58%), m.p. 90 °C (ether), homogeneous by g.l.c. on column A (R_t 27 min) at 220 °C (Found: C, 71.4; H, 7.35. $C_{18}H_{22}O_4$ requires C, 71.5; H, 7.35%); $\nu_{max.}$(KBr) 3 000, 2 945, 2 880, 2 830, 1 725, 1 705, 1 605, 1 500, 1 440, 1 310, 1 240, 1 210, 1 120, 1 040, 1 030, 860, and 815 cm^{-1}; $\delta_H(CDCl_3)$ 1.40—3.21 (13 H, m), 3.50 (3 H, s, CO_2Me), 3.80 (3 H, s, ArOMe), and 6.50—7.2 (3 H, m, ArH); $\delta_C(CDCl_3)$ 209.4 (s, C-2), 171.7 (s, C-12), 157.1 (s, C-6), 142.3 (s, C-4b), 130.0 (d, C-8), 126.9 (s, C-8a), 112.4 (d, C-5), 111.1 (d, C-7), 55.0 (q, ArOMe), 51.1 (q, Me ester), 44.0 (t, C-1), 43.0 (d, C-10a), 38.5 (s, C-4a), 37.8 (t, C-3), 36.2 (t, C-11), 33.6 (t, C-4), 27.4 (t, C-9), and 24.8 p.p.m. (t, C-10).

Catalytic Hydrogenation of the Unsaturated Keto-ester (**13b**) *to Products* (**14b**) *and* (**15b**).—The unsaturated keto-ester (**13b**) (500 mg, 1.7 mmol) was hydrogenated in DMF (10 ml) in the presence of 10% Pd–C (45 mg). After the catalyst had been filtered off, the filtrate was diluted with water and extracted with ether to afford a thick colourless liquid (500 mg, 99%), which was found to be a mixture of the *cis*- and the *trans*-keto-esters (**14b**) and (**15b**) in the ratio 2:1 (from ^1H n.m.r. and g.l.c.).

cis-*Methyl* 5-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (**14c**).—The unsaturated keto-ester (**13c**) (3 g, 10 mmol) was hydrogenated in dry pyridine (60 ml) in the presence of 10% Pd–C (180 mg) in a manner similar to that used for (**13b**) to give, after similar work-up, the solid *cis*-keto-ester (**14c**) (3 g, 99%), *ca.* 96% pure by g.l.c. and ^1H n.m.r. analyses. This material, on recrystallization from light petroleum, gave pure *compound* (**14c**) (2.8 g, 93%), m.p. 74 °C, homogeneous by g.l.c. on column A (R_t 22.4 min) at 220 °C (Found: C, 71.55; H, 7.6. $C_{18}H_{22}O_4$ requires C, 71.5; H, 7.35%); $\nu_{max.}$(KBr) 3 000, 2 950, 2 930, 2 860, 1 720, 1 710, 1 595, 1 470, 1 430, 1 350, 1 250, 1 210, 1 180, 1 080, 995, 940, 790, and 755 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—2.66 (9 H, m), 2.83 (2 H, t, *J* 6 Hz, $ArCH_2$), 3.10 (2 H, d, *J* 4 Hz, $COCH_2$), 3.51 (3 H, s, CO_2Me), 3.80 (3 H, s, ArOMe), and 6.50—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 211.4 (s, C-2), 171.8 (s, C-12), 158.3 (s, C-5), 137.9 (s, C-8a), 128.2 (s, C-4b), 126.9 (d, C-7), 122.1 (d, C-8), 108.8 (d, C-6), 54.8 (q, ArOMe), 50.9 (q, Me ester), 43.3 (t, C-1), 40.6 (t, C-11), 39.9 (d, C-10a), 39.6 (s, C-4a), 37.6 (t, C-3), 32.7 (t, C-4), 27.9 (t, C-9), and 24.8 p.p.m. (t, C-10).

trans-*Methyl* 5-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (**15c**).—*Method A*. The unsaturated keto ester (**13c**) (3 g, 10 mmol) was hydrogenated in DMF (75 ml) in the presence of 10% Pd–C (200 mg), as described for (**13b**), to afford a mixture of the *trans*- and *cis*-keto-esters (**14c**) and (**15c**) in the ratio *ca.* 86:14 (^1H n.m.r. and g.l.c.). Recrystallization twice from ether–light petroleum (1:1) afforded the pure trans-*epimer* (**15c**) (2.2 g, 73%), m.p. 102 °C, homogeneous on g.l.c. on column A (R_t 24.6 min) at 220 °C (Found: C, 71.4; H, 7.45. $C_{18}H_{22}O_4$ requires C, 71.5; H, 7.35%); $\nu_{max.}$(KBr) 3 020, 3 000, 2 950, 2 930, 2 880, 2 830, 1 725, 1 705, 1 600, 1 575, 1 465, 1 450, 1 430, 1 335, 1 300, 1 260, 1 200, 1 155, 1 085, 1 070, 1 020, 930, 880, 780, and 705 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—3.20 (13 H, m), 3.49 (3 H, s, CO_2Me), 3.73 (3 H, s, ArOMe), and 6.53—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 210.0 (s, C-2), 172.1 (s, C-12), 158.5 (s, C-5), 137.9 (s, C-8a), 129.4 (s, C-4b), 127.0 (d, C-7), 122.1 (d, C-8), 108.3 (d, C-6), 54.5 (q, ArOMe), 50.8 (q, Me ester), 44.6 (d, C-10a), 44.2 (t, C-1), 39.7 (s, C-4a), 38.0 (t, C-3), 35.5 (t, C-11), 34.1 (t, C-4), 30.2 (t, C-9), and 24.7 p.p.m. (t, C-10).

Method B. The keto-lactone (**12c**) (1.3 g, 4.5 mmol) was converted into the lithium salt (**16c**) and reduced with Li–NH_3 in the same way as for the compound (**12b**), to give, after an identical sequence of reactions and work-up, a mixture of the epimeric *cis*- and *trans*-keto-esters (**14c**) and (**15c**) (900 mg, 66%) in the ratio *ca.* 18:82 (^1H n.m.r. and g.l.c.). Recrystallization three times from ether–light petroleum gave the pure *trans*-compound (**15c**) (*ca.* 600 mg, 44%), m.p. and mixed m.p. 112 °C.

cis-*Methyl* 2,2-*Ethylenedioxy*-6-*methoxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (**17b**).—The *cis*-keto-ester (**14b**) (2 g, 6.6 mmol) and ethylene glycol (1.25 ml, 22.4 mmol) in dry benzene (60 ml) containing toluene-*p*-sulphonic acid (100 mg) was refluxed for 20 h under N_2 using a Dean and Stark water separator. The reaction mixture was cooled and poured into water (100 ml) containing KOH (50 mg). The benzene layer and two extracts from the aqueous layer were washed with water, dried, and evaporated to give the acetal ester (**17b**) (2.1 g, 92%) as a thick colourless oil; $\nu_{max.}$(neat) 2 940, 2 860, 1 730, 1 605, 1 570, 1 500, 1 460, 1 440, 1 290, 1 240, 1 160, 1 090, and

1 050 cm^{-1}; $\delta_H(CDCl_3)$ 1.23—3.00 (13 H, m), 3.60 (3 H, s, CO_2Me), 3.76 (3 H, s, ArOMe), 3.90 (4 H, s, OCH_2CH_2O), and 6.53—7.06 (3 H, m, ArH). As this compound was found to be relatively unstable it was directly reduced with $LiAlH_4$.

cis-*Methyl* 2,2-*Ethylenedioxy*-5-*methoxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*ylacetate* (**17c**).—The *cis*-keto-ester (**14c**) (2 g, 6.6 mmol) was treated as described above to give the acetal ester (**17c**) (2 g, 87%) as a thick colourless oil; $\nu_{max.}$(neat) 2 940, 2 880, 2 840, 1 725, 1 600, 1 575, 1 465, 1 435, 1 340, 1 250, 1 150, 1 100, and 1 080 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—3.16 (13 H, m), 3.50 (3 H, s, CO_2Me), 3.77 (3 H, s, ArOMe), 3.91 (4 H, s, OCH_2CH_2O), and 6.50—7.26 (3 H, m, ArH). As this compound was found to be relatively unstable it was directly reduced with $LiAlH_4$.

trans-*Methyl* 2,2-*Ethylenedioxy*-6-*methoxy*-1,2,3,4,4a,9,-10,10a-*octahydrophenanthren*-4a-*ylacetate* (**18b**). —The *trans*-keto-ester (**15b**) (2 g, 6.6 mmol) was treated as described above to afford the trans-*acetal ester* (**18b**) (2.1 g, 92%), m.p. 132 °C (dichloromethane–petroleum) (Found: C, 69.3; H, 7.7. $C_{20}H_{26}O_5$ requires C, 69.35; H, 7.55%); $\nu_{max.}$(KBr) 2 990, 2 940, 2 920, 2 840, 2 800, 1 725, 1 610, 1 500, 1 450, 1 430, 1 315, 1 240, 1 200, 1 100, 950, 855, and 825 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—3.03 (13 H, m), 3.46 (3 H, s, CO_2Me), 3.76 (3 H, s, ArOMe), 3.96 (4 H, s, OCH_2CH_2O), and 6.50—7.26 (3 H, m, ArH).

trans-*Methyl* 2,2-*Ethylenedioxy*-5-*methoxy*-1,2,3,4,4a,9,-10,10a-*octahydrophenanthren*-4a-*ylacetate* (**18c**).—The *trans*-keto-ester (**15c**) (2 g, 6.6 mmol) was treated as described above to give the acetal ester (**18c**) (2.05 g, 89.5%), m.p. 95 °C (ether–light petroleum) (Found: C, 69.4; H, 7.65. $C_{20}H_{26}O_5$ requires C, 69.35; H, 7.55%); $\nu_{max.}$(KBr) 3 020, 2 940, 2 860, 2 820, 1 730, 1 600, 1 575, 1 460, 1 430, 1 300, 1 260, 1 250, 1 210, 1 100, 1 080, 1 065, 1 030, 1 005, 960, 950, 810, 780, and 745 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—3.23 (13 H, m), 3.43 (3 H, s, CO_2Me), 3.70 (3 H, s, ArOMe), 3.91 (4 H, s, OCH_2CH_2O), and 6.50—7.26 (3 H, m, ArH).

cis-2-(2,2-*Ethylenedioxy*-6-*methoxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**19b**).—A solution of the *cis*-acetal ester (**17b**) (2 g, 5.8 mmol) in dry ether (50 ml) was added to a stirred slurry of $LiAlH_4$ (700 mg, 17.5 mmol) in dry ether (50 ml), and the reaction mixture was refluxed for 4 h. Usual work-up afforded the *cis*-acetal alcohol (**19b**) (1.8 g, 98%), b.p. 215—220 °C (0.1 mmHg) (Found: C, 71.7; H, 8.55. $C_{19}H_{26}O_4$ requires C, 71.65; H, 8.25%); $\nu_{max.}$(neat) 3 420, 2 940, 2 880, 1 610, 1 570, 1 500, 1 470, 1 360, 1 290, 1 240, 1 160, 1 100, 1 040, and 950 cm^{-1}; $\delta_H(CDCl_3)$ (100 MHz) 1.24—2.48 (12 H, m), 2.60—2.84 (2 H, m, $ArCH_2$), 3.56 (2 H, t, *J* 6 Hz, CH_2OH), 3.72 (3 H, s, ArOMe), 3.86 (4 H, s, OCH_2CH_2O), and 6.60—7.28 (3 H, m, ArH); $\delta_C(CDCl_3)$ 157.4 (s, C-6), 141.2 (s, C-4b), 130.3 (d, C-8), 127.8 (s, C-8a), 111.7 and 111.0 (d, C-5 and C-7), 109.0 (s, C-2), 63.9 (t, OCH_2CH_2O), 58.7 (t, C-12), 55.1 (q, ArOMe), 45.1 (t, C-11), 39.2 (s, C-4a), 36.7 (d, C-10a), 36.3 (t, C-1), 31.6 and 31.0 (t, C-3 and C-4), 24.4 (t, C-9), and 23.1 p.p.m. (t, C-10).

cis-2-(2,2-*Ethylenedioxy*-5-*methoxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**19c**).—A solution of the *cis*-acetal ester (**17c**) (2 g, 5.8 mmol) in dry ether was reduced with $LiAlH_4$ (700 mg, 17.5 mmol) as above to afford the cis-*acetal alcohol* (**19c**) (1.75 g, 95%), b.p. 200—210 °C (0.05 mmHg) (Found: C, 71.55; H, 8.55. $C_{19}H_{26}O_4$ requires C, 71.65; H, 8.25%); $\nu_{max.}$(neat) 3 400, 2 940, 2 880, 1 595, 1 575, 1 450, 1 350, 1 290, 1 250, 950, 910, 780, and 750 cm^{-1}; $\delta_H(CDCl_3)$ 1.23—2.58 (12 H, m), 2.60—2.93 (2 H, m, $ArCH_2$), 3.53 (2 H, t, *J* 7 Hz, CH_2OH), 3.76 (3 H, s, ArOMe), 3.91 (4 H, s, OCH_2CH_2O), and 6.50—7.30 (3 H, m, ArH); $\delta_C(CDCl_3)$ 158.8 (s, C-5), 138.5 (s, C-4b), 129.2 (s, C-8a), 126.1 (d, C-7), 122.3 (d, C-8), 108.8 (s, C-2), 108.6 (d, C-6), 63.8 (t, OCH_2CH_2O), 59.5 (t, C-12), 54.7 (q, ArOMe), 40.5 (t, C-11), 39.6 (s, C-4a), 38.7 (s, C-10a), 36.5 (t, C-1), 31.3 and 30.9 (t, C-3 and C-4), 27.9 (t, C-9), and 24.1 p.p.m. (t, C-10).

trans-2-(2,2-*Ethylenedioxy*-6-*methoxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**20b**).—A solution of the *trans*-acetal ester (**18b**) (1 g, 2.9 mmol) in dry ether was reduced with $LiAlH_4$ (350 mg, 8.8 mmol) as described above to yield the *acetal alcohol* (**20b**) (890 mg, 97%), b.p. 215—220 °C (0.1 mmHg) (Found: C, 71.8; H, 8.4. $C_{19}H_{26}O_4$ requires C, 71.65; H, 8.25%); $\nu_{max.}$(neat) 3 420, 2 940, 2 880, 1 600, 1 575, 1 495, 1 365, 1 100, 1 080, 1 040, and 945 cm^{-1}; $\delta_H(CDCl_3$; 100 MHz) 1.40—2.48 (12 H, m), 2.60—3.00 (2 H, m, $ArCH_2$), 3.32—3.68 (2 H, m, CH_2OH), 3.72 (3 H, s, ArOMe), 3.88 (4 H, s, OCH_2CH_2O), and 6.52—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 156.8 (s, C-6), 145.3 (s, C-4b), 130.1 (d, C-8), 127.5 (s, C-8a), 111.4 and 111.1 (d, C-5 and C-7), 108.6 (s, C-2), 64.1 and 64.0 (t, OCH_2CH_2O), 59.2 (t, C-12), 55.1 (q, ArOMe), 39.9 (s, C-10a), 37.9 (t, C-1), 37.6 (s, C-4a), 32.3 (t, C-11), 31.1 (t, C-3 and C-4), 26.9 (t, C-9), and 24.5 p.p.m. (t, C-10).

trans-2-(2,2-*Ethylenedioxy*-5-*methoxy*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**20c**).—A solution of the *trans*-acetal ester (**18c**) (2 g, 5.8 mmol) was reduced with $LiAlH_4$ in ether as described above to afford the *acetal alcohol* (**20c**) (1.73 g, 94%), b.p. 195—200 °C (0.05 mmHg) (Found: C, 71.7; H, 8.1. $C_{19}H_{26}O_4$ requires C, 71.65; H, 8.25%); $\nu_{max.}$(neat) 3 400, 2 940, 2 880, 1 595, 1 570, 1 460, 1 445, 1 360, 1 245, 1 140, 1 080, 1 020, 950, 790, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—2.33 (11 H, m), 2.66—3.30 (3 H, m, $ArCH_2$), 3.50 (2 H, t, *J* 7 Hz, CH_2OH), 3.76 (3 H, s, ArOMe), 3.93 (4 H, s, OCH_2CH_2O), and 6.50—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 158.5 (s, C-5), 138.4 (s, C-8a), 131.7 (s, C-4b), 126.2 (d, C-7), 122.3 (d, C-8), 108.6 (d, C-6), 108.3 (s, C-2), 63.7 and 63.6 (t, OCH_2CH_2O), 60.4 (t, C-12), 54.7 (q, ArOMe), 41.7 (d, C-10a), 38.8 (s, C-4a), 38.1 (t, C-1), 33.6 (t, C-11), 32.2 and 31.1 (t, C-3 and C-4), 29.7 (t, C-9), and 25.0 p.p.m. (t, C-10).

cis-2-(2-*Oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**21a**).—A mixture of the *cis*-acetal alcohol (**19a**)[1] (2 g, 6.9 mmol) in methanol (10 ml) and 3M-HCl (2.5 ml) was heated on a steam-bath for 1 h, cooled, the methanol removed under reduced pressure, and the reaction mixture then diluted with water and extracted with ether. The ethereal layer was washed with brine, dried, and the solvent removed to afford the *keto-alcohol* (**21a**) (1.5 g, 88%), b.p. 165—170 °C (0.2 mmHg) (Found: C, 78.65; H, 8.55. $C_{16}H_{20}O_2$ requires C. 78.65; H, 8.25%); $\nu_{max.}$(neat) 3 420, 2 920, 2 880, 1 705, 1 440, 1 030, 760, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 1.40—2.56 (12 H, m, OH at δ 1.73 exchangeable with D_2O), 2.86 (2 H, t, *J* 6 Hz, $ArCH_2$), 3.60 (2 H, t, *J* 7 Hz, CH_2OH), and 7.06—7.26 (4 H, m, ArH); $\delta_C(CDCl_3)$ 212.1 (s, C-2), 139.7 (s, C-4b), 135.6 (s, C-8a), 129.8 (d, C-8), 126.1 (d, C-6 and C-7), 126.0 (d, C-5), 58.7 (t, C-12), 43.6 (t, C-1), 43.1 (t, C-11), 40.0 (d, C-10a), 39.2 (s, C-4a), 37.9 (t, C-3), 35.6 (t, C-4), 26.2 (t, C-9), and 24.2 p.p.m. (t, C-10).

cis-2-(6-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**21b**).—The *cis*-acetal alcohol (**19b**) (2 g, 6.28 mmol) was deacetalized with methanolic HCl according to the above method to yield the *keto-alcohol* (**21b**) (1.5 g, 87%), b.p. 185—190 °C (0.05 mmHg) (Found: C, 74.75; H, 8.15. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.1%); $\nu_{max.}$(neat) 3 400, 2 920, 2 840, 1 705, 1 610, 1 570, 1 500, 1 460, 1 280, 1 240, 1 180, and 1 040 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—3.00 (14 H, m, OH at δ 2.03 exchangeable with D_2O), 3.61 (2 H, t, *J* 7 Hz, CH_2OH), 3.80 (3 H, s, ArOMe), and 6.56—7.26 (3 H, m, ArH); $\delta_C(CDCl_3)$ 211.9 (s, C-2), 157.7 (s, C-6), 140.8 (s, C-4b), 130.5 (d, C-8), 127.5 (s,

C-8a), 111.7 and 111.3 (d, C-5 and C-7), 58.6 (t, C-12), 55.0 (q, ArOMe), 43.4 (t, C-1), 42.9 (t, C-11), 37.9 (d, C-10a), 39.2 (s, C-4a), 37.7 (t, C-3), 35.5 (t, C-4), 25.2 (t, C-9), and 24.1 p.p.m. (t, C-10).

cis-2-(5-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**21c**).—The *cis*-acetal alcohol (**19c**) (2 g, 6.28 mmol) was deacetalized according to the method described above to yield the *keto-alcohol* (**21c**) (1.5 g, 87%), b.p. 195—200 °C (0.05 mmHg) (Found: C, 74.2; H, 8.0. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.1%); $\nu_{max.}$(neat) 3 400, 2 940, 2 840, 1 700, 1 600, 1 575, 1 465, 1 450, 1 250, and 1 080 cm^{-1}; $\delta_H(CDCl_3)$ 1.23—3.00 (14 H, m, OH at δ 1.73 exchangeable with D_2O), 3.55 (2 H, t, *J* 7 Hz, CH_2OH), 3.83 (3 H, s, ArOMe), and 6.50—7.36 (3 H, m, ArH); $\delta_C(CDCl_3)$ 212.6 (s, C-2), 158.5 (s, C-5), 138.1 (s, C-8a), 128.6 (s, C-4b), 126.7 (d, C-7), 122.3 (d, C-8), 108.7 (d, C-6), 59.6 (t, C-12), 54.8 (q, ArOMe), 44.0 (t, C-1), 41.5 (d, C-10a), 39.4 (s, C-4a), 38.9 (t, C-11), 37.8 (t, C-3), 33.5 (t, C-4), 28.6 (t, C-9), and 25.2 p.p.m. (t, C-10).

trans-2-(2-*Oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**22a**).—The *trans*-acetal alcohol (**20a**) (2 g, 6.9 mmol) was similarly deacetalized with methanolic HCl to afford the *keto-alcohol* (**22a**) (1.54 g, 91%), m.p. 134 °C (ethyl acetate–petroleum) (Found: C, 78.45; H, 8.55. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%); $\nu_{max.}$(KBr) 3 405, 2 940, 2 880, 1 700, 1 490, 1 450, 1 350, 1 240, 1 210, 1 060, 1 040, 1 020, 770, 730, and 705 cm^{-1}; $\delta_H(CDCl_3)$ 1.40—3.06 (14 H, m, OH at δ 1.73 which disappeared on deuteriation), 3.61 (2 H, t, *J* 7 Hz, CH_2OH), and 7.13 (4 H, br s, ArH); $\delta_C(CDCl_3)$ 211.2 (s, C-2), 142.5 (s, C-4b), 135.5 (s, C-8a), 129.6 (d, C-8), 126.3 (d, C-7), 125.6 (d, C-6), 125.1 (d, C-5), 58.9 (t, C-12), 44.2 (t, C-1), 43.2 (d, C-10a), 37.9 (t, C-3), 37.6 (s, C-4a), 33.9 (t, C-4), 32.7 (t, C-11), 27.9 (t, C-9), and 24.8 p.p.m. (t, C-10).

trans-2-(6-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**22b**).—A mixture of the *trans*-acetal alcohol (**20b**) (900 mg, 2.8 mmol) in methanol (4.5 ml) and 3M-HCl (1 ml) was treated as above to yield the *keto-alcohol* (**22b**) (750 mg, 97%), m.p. 150 °C (ethyl acetate–petroleum) (Found: C, 74.0; H, 8.2. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.1%); $\nu_{max.}$(KBr) 3 480, 2 940, 2 890, 2 840, 1 700, 1 610, 1 580, 1 490, 1 450, 1 420, 1 290, 1 200, 1 030, 860, and 830 cm^{-1}; $\delta_H(CDCl_3)$ 1.48—3.00 (14 H, m), 3.61 (2 H, t, *J* 7 Hz, CH_2OH), 3.74 (3 H, s, ArOMe), and 6.60—7.08 (3 H, m, ArH); $\delta_C(CDCl_3)$ 210.9 (s, C-2), 156.9 (s, C-6), 143.6 (s, C-4b), 130.2 (d, C-8), 127.5 (s, C-8a), 111.7 and 111.4 (d, C-5 and C-7), 58.9 (t, C-12), 55.0 (q, ArOMe), 44.0 (t, C-1), 43.0 (d, C-10a), 37.7 (t, C-3 and C-4a), 33.8 (t, C-4), 32.5 (t, C-11), 26.9 (t, C-9), and 24.8 p.p.m. (t, C-10).

trans-2-(5-*Methoxy*-2-*oxo*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-4a-*yl*)*ethanol* (**22c**).—The *trans*-acetal alcohol (**20c**) (2 g, 6.28 mmol) was deacetalized with methanolic HCl according to the aforementioned method to afford the *keto-alcohol* (**22c**) (1.54 g, 91%), b.p. 200—210 °C (0.05 mmHg) (Found: C, 74.45; H, 8.0. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.1%); $\nu_{max.}$(neat) 3 400, 2 940, 2 880, 2 840, 1 705, 1 600, 1 570, 1 470, 1 420, 1 250, 1 200, 1 080, 910, 780, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 1.17—2.70 (12 H, m, OH at δ 1.87 exchangeable with D_2O), 2.73—3.03 (2 H, m, $ArCH_2$), 3.33—3.66 (2 H, m, CH_2OH), 3.77 (3 H, s, ArOMe), and 6.50—7.36 (3 H, m, ArH); $\delta_C(CDCl_3)$ 211.5 (s, C-2), 158.5 (s, C-5), 138.2 (s, C-8a), 130.0 (s, C-4b), 126.8 (d, C-7), 122.3 (d, C-8), 108.7 (d, C-6), 60.4 (t, C-12), 54.8 (q, ArOMe), 44.7 (d, C-10a), 44.4 (t, C-3), 34.9 (t, C-4), 33.9 (t, C-11), 29.9 (t, C-9), and 25.2 p.p.m. (t, C-10).

cis-4a-(2-*Methylsulphonyloxyethyl*)-3,4,4a,9,10,10a-*hexahydrophenanthren*-2(1H)-*one* (**5a**).—A solution of the *cis*-keto-alcohol (**21a**) (1.5 g, 6.15 mmol) and dry pyridine 2.5 ml) in dry dichloromethane (15 ml) was kept at −10 to −7 °C and methanesulphonyl chloride (0.80 ml, 10.5 mmol) was added dropwise. The reaction mixture was left overnight at −10 °C, then mixed with ice–water (20 ml) and extracted with dichloromethane. The combined extracts were washed with water, dried, and evaporated. The residue in benzene solution was rapidly filtered through a neutral alumina column. Benzene elution afforded the *methanesulphonate* (**5a**) (1.65 g, 83%), m.p. 98 °C (ethyl acetate–petroleum) (Found: C, 63.4; H, 6.95. $C_{17}H_{22}O_4S$ requires C, 63.35; H, 6.9%); $\nu_{max.}$(KBr) 3 020, 2 930, 2 880, 1 700, 1 490, 1 450, 1 420, 1 350, 1 075, 970, 835, and 780 cm^{-1}; $\delta_H(CDCl_3)$ 1.76—2.56 (11 H, m), 2.83 (2 H, t, *J* 6 Hz, $ArCH_2$), 2.93 (3 H, s, OSO_2CH_3), 4.16 (2 H, t, *J* 7 Hz, CH_2OSO_2), and 7.10—7.26 (4 H, m, ArH).

trans-4a-(2-*Methylsulphonyloxyethyl*)-3,4,4a,9,10,10a-*hexahydrophenanthren*-2(1H)-*one* (**6a**).—A solution of the *trans*-keto-alcohol (**22a**) (1.5 g, 6.15 mmol) and dry pyridine (2.5 ml) in dry dichloromethane was treated with methanesulphonyl chloride (0.80 ml, 10.5 mmol) as described above. The crude methanesulphonate in benzene solution was rapidly filtered through a neutral alumina column to afford the solid *methanesulphonate* (**6a**) (1.7 g, 86%), m.p. 137 °C (ether) (Found: C, 63.1; H, 6.8. $C_{17}H_{22}O_4S$ requires C, 63.35; H, 6.9%); $\nu_{max.}$(KBr) 3 020, 2 940, 2 920, 2 860, 1 700, 1 490, 1 450, 1 420, 1 350, 1 335, 1 180, 935, 915, 800, and 760 cm^{-1}; $\delta_H(CDCl_3)$ 1.40—2.66 (11 H, m), 2.93 (5 H, m, OSO_2CH_3,$ArCH_2$), 4.03—4.33 (2 H, m, CH_2OSO_2), and 7.16 (4 H, br s, ArH).

Intramolecular Alkylation Reactions of the cis-*Keto-methanesulphonate* (**5a**). cis-3,4,4a,9,10,10a-*Hexahydro*-1,4a-*ethanophenanthren*-2(1H)-*one* (**23a**) *and* cis-3,4,4a,9,10,10a-*Hexahydro*-3,4a-*ethanophenanthren*-2(1H)-*one* (**24a**).—(A) *With* NaH. A solution of the *cis*-keto-methanesulphonate (**5a**) (500 mg, 1.55 mmol) in dry benzene (10 ml) was added at ambient temperature with efficient stirring to a suspension of NaH (240 mg, 10 mmol) in dry benzene (10 ml) under N_2. The resulting mixture was treated under reflux with stirring for 12 h, then cooled and acidified with cold 6M-HCl. The benzene layer was separated and the aqueous layer was extracted with benzene. The combined benzene layers were washed with water, dried, and solvent removed. The crude product was chromatographed on neutral alumina. Benzene–petroleum (1:1) elution afforded the alkylated product (200 mg, 57%), b.p. 160—165 °C (bath temp.) (0.1 mmHg); g.l.c. analysis showed it to be a mixture of the regioisomeric bridged ketones (**23a**) and (**24a**) in the ratio *ca.* 3:1, with R_t 21.84 and 24.66 min, respectively, in column B at 130 °C (Found: C, 84.95; H, 8.1. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%); $\nu_{max.}$(neat) 2 940, 2 870, 1 710, 1 485, 1 450, 1 420, 1 230, 1 160, 1 130, and 760 cm^{-1}; $\delta_H(CCl_4)$ 1.33—3.03 (14 H, m) and 7.00 (4 H, br, s, ArH); *m/z* 226 (M^+, 31%), 197 (10), 169 (93), 143 (24), 142 (72), 141 (100), 129 (48), 128 (97), and 115 (86). ^{13}C N.m.r. data: for (**23a**) from the mixture; $\delta_C(CDCl_3)$ 214 (s, C-2), 144.6 (s, C-4b), 134.8 (s, C-8a), 128.9 (d, C-8), 125.9 (d, C-6 and C-7), 125.6 (d, C-5), 53.8 (d, C-1), 49.6 (d, C-10a), 44.0 (s, C-4a), 37.3 (t, C-3), 34.6 and 33.3 (t, C-4 and C-11), 28.9 (t, C-12), 27.8 (t, C-9), and 20.5 p.p.m. (t, C-10); those discernible for the minor epimer (**24a**) from the mixture; δ_C* 52.2, 46.9, 44.0, 43.3, 42.3, 38.2, 30.6, 28.7, and 28.3 p.p.m.

(B) *With alumina.* A solution of compound (**5a**) (1.98 g, 6.15 mmol) in dry CH_2Cl_2 (10 ml) was stirred over alumina (2 g) at room temperature (25—30 °C) for 24 h. The mixture was then left for 48 h, the solvent evaporated under reduced pressure on a

* The aromatic carbons and the C=O signals for (**24a**) were overlapped with those of the major isomer (**23a**).

steam-bath, and the residue dried for 1 h at 40—45 °C (10 mmHg), and charged on a prepacked column of alumina (20 g). It was eluted with benzene–petroleum (200 ml; 1:1) to afford a 3:1 mixture of (**23a**) and (**24a**) (750 mg, 54%) as shown by g.l.c. This mixture was identical in all respects (g.l.c., i.r., and ^{13}C n.m.r.) with the product described above.

(C) *With* Bu^{t}OK–Bu^{t}OH: cis-3-*hydroxy*-4a,9,10,10a-*tetrahydro*-1,4a-*ethanophenanthren*-2(1H)-*one* (**25**). (i) To a solution of Bu^{t}OK (347 mg, 3.1 mmol) in dry Bu^{t}OH (30 ml) under N_2 was added a solution of compound (**5a**) (500 mg, 1.55 mmol) in dry Bu^{t}OH (25 ml) and the resulting solution was stirred at room temperature for 20 h, then poured onto ice-cold 0.1M-HCl and the resulting mixture extracted thoroughly with ether. The combined ethereal extracts were washed with water, dried, and the solvent removed. The crude product was chromatographed on silica gel (15 g) and elution with benzene–petroleum (1:1) afforded the *enolic* α-*diketone* (**25**) (180 mg, 48%), m.p. 156 °C (ether) (Found: C, 79.85; H, 6.9. $C_{16}H_{16}O_2$ requires C, 79.95; H, 6.7%); $\nu_{max.}$(KBr) 3 400, 3 050, 3 020, 2 950, 2 930, 2 860, 1 670, 1 640, 1 390, 1 370, 1 260, 1 245, 1 195, 1 160, 1 100, 1 080, 960, 860, 760, 750, 720, and 640 cm^{-1}; δ_H($CDCl_3$) 1.50—3.20 (10 H, m), 5.86 (1 H, d, *J* 2 Hz, C*H*=COH), and 7.0—7.33 (4 H, m, ArH). The enolic OH could not be detected, possibly owing to rapid exchange; δ_C($CDCl_3$) 197.1 (s, C-2), 144.7 (s, C-3), 142.4 (s, C-4b), 136.0 (s, C-8a), 128.8 (d, C-8), 126.6 (d, C-5, C-6, and C-7), 125.0 (d, C-4), 52.8 (d, C-10a), 51.0 (d, C-1), 48.1 (s, C-4a), 35.0 (t, C-11), 29.5 (t, C-9), 25.9 (t, C-12), and 20.3 p.p.m. (t, C-10); *m/z* 240 (M^+, 100%), 212 (77.5), 211 (62), 184 (79), 183 (62), 169 (35), 165 (39), 142 (37), 141 (57), 129 (31.5), 128 (43), and 115 (38).

A trace of a thick liquid contaminated with compound (**25**), eluted in one of the earlier chromatographic fractions, showed a C=O band at 1 710 cm^{-1} in the i.r. spectrum, which was not characterized further.

(ii) To a solution of Bu^{t}OK (112 mg, 1 mmol) in dry Bu^{t}OH (10 ml) under N_2 was added a solution of a 3:1 mixture of (**23a**) and (**24a**) (113 mg, 0.05 mmol) in dry Bu^{t}OH (5 ml) and the resulting solution was stirred at room temperature for 20 h. Work-up as above afforded a reddish brown gummy residue (80 mg) which, on chromatography over silica gel, gave a colourless thick liquid (50 mg) ($\nu_{max.}$ 3 400, 1 710w, and 1 670s cm^{-1}). This, on recrystallization from ether, gave compound (**25**) (*ca.* 20 mg, 8%), m.p. and mixed m.p. 156 °C.

Intramolecular Alkylation Reactions of the trans-*Keto-methanesulphonate* (**6a**). trans-3,4,4a,9,10,10a-*Hexahydro*-3,4a-*ethanophenanthren*-2(1H)-*one* (**26a**).—(A) *With* NaH. The *trans*-keto-methanesulphonate (**6a**) (500 mg, 1.55 mmol) in dry benzene (10 ml) was treated with NaH (240 mg, 10 mmol) in the same way as for compound (**5a**) to give the crude product, which on chromatography over alumina using benzene–petroleum (1:1) as eluant gave the *bridged ketone* (**26a**) (205 mg, 58%) as a glassy solid, homogeneous on g.l.c. (R_t 5.43 min), column B at 180 °C. This was triturated with ether–light petroleum and then left in the ice-box for several weeks to give a solid, m.p. 180 °C (ether–light petroleum) (Found: C, 85.15; H, 8.25. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%); $\nu_{max.}$(KBr) 2 930, 2 880, 1 720, 1 490, 1 450, 1 415, 1 245, 1 210, 1 125, 790, 760, 730, and 700 cm^{-1}; δ_H($CDCl_3$) 1.33—3.00 (14 H, m) and 6.93—7.43 (4 H, m, ArH); δ_C($CDCl_3$) 212.4 (s, C-2), 140.8 (s, C-4b), 136.6 (s, C-8a), 129.0 (d, C-8), 126.0 (d, C-7), 125.8 (d, C-5 and C-6), 51.8 (d, C-3), 46.3 (s, C-4a), 44.8 (t, C-1 or C-4), 43.7 (d, C-10a), 42.3 (t, C-1 or C-4), 35.6 (t, C-11), 30.0 (t, C-9), 29.0 (t, C-12), and 26.0 (t, C-10); *m/z* 226 (M^+, 50%), 184 (75), 167 (25), 156 (50), 155 (37.5), 143 (35), 142 (45), 141 (75), 129 (50), 128 (100), and 115 (20).

(B) *With* Bu^{t}OK–Bu^{t}OH. Compound (**6a**) (500 mg, 1.55 mmol) was alkylated by treatment with Bu^{t}OK (347 mg, 3.1 mmol) in dry Bu^{t}OH (55 ml) as described for (**5a**) and, after chromatography on alumina, afforded the bridged-ketone (**26a**) (215 mg, 61%) as a glassy solid (homogeneous by g.l.c. and ^{13}C n.m.r.) which was crystallized from ether–light petroleum, m.p. and mixed m.p. 108 °C.

(C) *With alumina.* A solution of compound (**6a**) (1.98 g, 6.15 mmol) in dry CH_2Cl_2 (10 ml) was stirred over alumina (2 g) at room temperature for 24 h. After evaporation of the solvent and drying under reduced pressure (10 mmHg), the residue was charged on a prepacked alumina (20 g) column and eluted with benzene–petroleum (1:1) to afford the product (**26a**) (760 mg, 55%), m.p. and mixed m.p. 108 °C.

Intramolecular Alkylation Reactions of the cis- *and* trans-*Keto-methanesulphonates* (**5b**) *and* (**6b**) *with Alumina.* cis-6-*Methoxy*-3,4,4a,9,10,10a-*hexahydro*-1,4a-*ethanophenanthren*-2(1H)-*one* (**23b**) *and* cis-6-*Methoxy*-3,4,4a,0,10,10a-*hexahydro*-3,4a-*ethanophenanthren*-2(1H)-*one* (**24b**).—The crude keto-methanesulphonate (**5b**), prepared from the *cis*-keto-alcohol (**21b**) (1 g, 3.64 mmol) in dry pyridine (1.5 ml) and CH_2Cl_2 (10 ml) with methanesulphonyl chloride (0.5 ml, 6.4 mmol) as for (**5a**), was dissolved in dry CH_2Cl_2 (10 ml) and stirred with alumina for 24 h at room temperature. After 48 h, the solvent was removed from the slurry, under reduced pressure and the residue dried for 1 h at 40—45 °C under reduced pressure (10 mmHg) and charged on a prepacked alumina (15 g) column. Elution with benzene–petroleum (3:1 v/v; 200 ml) afforded a mixture of the *bridged ketones* (**23b**) and (**24b**) (505 mg, 54%) in the ratio *ca.* 4:1, by g.l.c. on column A at 220 °C, R_t 15 and 16 min, respectively; b.p. 180—185 °C (bath temp.) (0.05 mmHg) (Found: C, 79.75; H, 8.0. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.85%); $\nu_{max.}$(neat) 2 940, 2 870, 2 840, 1 710, 1 600, 1 570, 1 500, 1 465, 1 290, and 1 030 cm^{-1}; δ_H($CDCl_3$) 1.30—3.03 (14 H, m), 3.73 (3 H, s, ArOMe), and 6.43—7.03 (3 H, m, ArH). ^{13}C N.m.r. data for (**23b**) from the mixture: δ_C($CDCl_3$) 213.9 (s, C-2), 157.3 (s, C-6), 145.6 (s, C-4b), 129.6 (d, C-8), 126.6 (s, C-8a), 111.4 and 111.3 (d, C-5 and C-7), 55.0 (q, ArOMe), 53.7 (d, C-1), 49.4 (d, C-10a), 44.1 (s, C-4a), 37.0 (t, C-3), 34.4 (t, C-4), 33.2 (t, C-11), 28.0 (t, C-12), 27.5 (t, C-9), and 20.5 p.p.m. (t, C-10); those discernible for the minor isomer (**24b**) from the mixture; δ_C 52.0, 46.6, 43.7, 43.0, 42.1, 38.1, 29.6, 28.5, and 28.3 p.p.m.; the other signals were overlapped with those of (**23b**).

trans-6-*Methoxy*-3,4,4a,9,10,10a-*hexahydro*-3,4a-*ethanophenanthren*-2(1H)-*one* (**26b**).—The crude *trans*-keto-methanesulphonate (**6b**), prepared from the keto-alcohol (**22b**) (650 mg, 2.37 mmol) in dry pyridine 1 ml) and dry CH_2Cl_2 (10 ml) with methanesulphonyl chloride (0.33 ml, 2.37 mmol) as above, was dissolved in dry CH_2Cl_2 (5 ml) and stirred with alumina (0.8 g) for 24 h at room temperature. The dried mixture was charged on a prepacked alumina (8 g) column and eluted with benzene–petroleum (3:1 v/v; 150 ml) to give the *bridged-ketone* (**26b**) (350 mg, 58%) as a colourless, homogeneous (g.l.c. and ^{13}C n.m.r.), glass which solidified with time in an ice-box, m.p. 89 °C (ether–light petroleum) (Found: C, 79.6; H, 8.1. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.85%); $\nu_{max.}$(KBr) 2 950, 2 860, 2 830, 1 705, 1 610, 1 580, 1 500, 1 465, 1 450, 1 440, 1 420, 1 315, 1 240, 1 215, 1 030, 850, and 810 cm^{-1}; δ_H($CDCl_3$; 100 MHz) 1.56—3.00 (14 H, m), 3.78 (3 H, s, ArOMe), and 6.58—7.10 (3 H, m, ArH); δ_C($CDCl_3$) 211.9 (s, C-2), 157.7 (s, C-6), 141.8 (s, C-4b), 129.6 (d, C-8), 128.5 (s, C-8a), 111.4 and 110.9 (d, C-5 and C-7), 54.8 (q, ArOMe), 51.5 (d, C-3), 46.3 (s, C-4a), 44.5 (t, C-1 or C-4), 43.4 (d, C-10a), 41.9 (t, C-1 or C-4), 35.2 (t, C-11), 28.9 (t, C-9), 28.7 (t, C-12), and 25.9 p.p.m. (t, C-10).

Intramolecular Alkylation of the trans-*Keto-methanesulphonate* (**6c**) *with Alumina.* trans-5-*Methoxy*-3,4,4a,9,10,10a-*hexahydro*-3,4a-*ethanophenanthren*-2(1H)-*one* (**26c**).—The crude *trans*-keto-methanesulphonate (**6c**), prepared from the *trans*-

keto-alcohol (**22c**) (1 g, 3.64 mmol) in dry pyridine (1.5 ml) and CH_2Cl_2 (10 ml) with methanesulphonyl chloride (0.5 ml, 6.4 mmol) as above, was dissolved in dry CH_2Cl_2 (10 ml) and stirred with alumina (1.5 g) for 24 h at room temperature. The dried mixture was charged on an alumina (15 g) column and eluted with benzene–petroleum (3:1 v/v; 200 ml) to afford the *bridged-ketone* (**26c**) (508 mg, 54%) as a colourless glass, homogeneous (g.l.c. and ^{13}C n.m.r.), which solidified with time in an ice-box, m.p. 102 °C (ether–light petroleum) (Found: C, 79.75; H, 7.95. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.85%); $\nu_{max.}$(KBr) 2 940, 2 920, 2 860, 1 710, 1 595, 1 575, 1 460, 1 440, 1 270, 1 245, 1 210, 1 110, 1 080, 1 050, 1 000, 920, 780, and 730 cm^{-1}; $\delta_H(CDCl_3)$ 1.33—2.46 (11 H, m), 2.53—3.00 (2 H, m, $ArCH_2$), 3.20—3.56 (1 H, m, COCH), 3.83 (3 H, s, ArOMe), and 6.56—7.16 (3 H, m, ArH); $\delta_C(CDCl_3)$ 212.8 (s, C-2), 158.2 (s, C-5), 138.9 (s, C-8a), 128.5 (s, C-4b), 126.3 (d, C-7), 121.8 (d, C-8), 108.4 (d, C-6), 54.7 (q, ArOMe), 52.3 (d, C-3), 46.1 (d, C-10a), 45.7 (s, C-4a), 42.2 and 41.2 (t, C-1 and C-4), 30.9 (t, C-9), 30.4 (t, C-11), 29.1 (t, C-12), and 25.4 p.p.m. (t, C-10).

cis-3,4,4a,9,10,10a-*Hexahydro*-5,4a-(*epoxyethano*)*phenanthren*-2(1H)-*one* (**27**).—Treatment of the *cis*-keto-alcohol (**21c**) (1 g, 3.64 mmol) in dry pyridine (1.5 ml) and dry CH_2Cl_2 (15 ml) with methanesulphonyl chloride (0.5 ml, 6.4 mmol) as described for (**5a**), after the usual work-up, gave a complex mixture of products, which exhibited only very weak signals at δ 2.83 (s) and 3.86 (s) in the ^1H n.m.r. corresponding to the OSO_2Me and OMe moieties. The crude product was dissolved in dry CH_2Cl_2 (10 ml) and stirred for 24 h at room temperature with alumina (1.5 g). The dried slurry was charged on an alumina (15 g) column and eluted with benzene–petroleum (3:1 v/v; 200 ml) to afford *compound* (**27**) (350 mg, 40%), m.p. 106 °C (ether–light petroleum), as the only isolable product (Found: C, 71.3; H, 6.2. $C_{16}H_{18}O_2$ requires C, 71.3; H, 6.35%); $\nu_{max.}$(KBr) 2 940, 2 880, 1 710, 1 600, 1 580, 1 470, 1 450, 1 260, 1 165, 1 080, 895, 780, and 740 cm^{-1}; δ_H (100 MHz; $CDCl_3$) 1.68—3.04 (m, 13 H), 4.3—4.56 (m, 2 H, CH_2O), and 6.56—7.32 (m, 3 H, ArH); $\delta_C(CDCl_3)$ 209.9 (s, C-2), 152.9 (s, C-5), 135.0 (s, C-8a), 127.1 (d, C-7), 125.2 (s, C-4b), 120.4 (d, C-8), 113.5 (d, C-6), 62.3 (t, C-12), 43.8 (t, C-1), 41.2 (d, C-10a), 36.8 (t, C-3), 32.1 (s, C-4a), 30.4 and 29.1 (t, C-4 and/or C-11), 27.4 (t, C-9), and 25.4 p.p.m. (t, C-10).

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