Acid-catalysed Intramolecular *C*-Alkylation in β,γ-Unsaturated Diazomethyl Ketones. Part 4.[1] Synthesis of Functionalised Hydrophenanthrene and Benzocyclodecenone Derivatives *via* Novel Fragmentation Reactions, and *X*-Ray Structural Analyses of Two Angularly Substituted Hydrophenanthrene Derivatives

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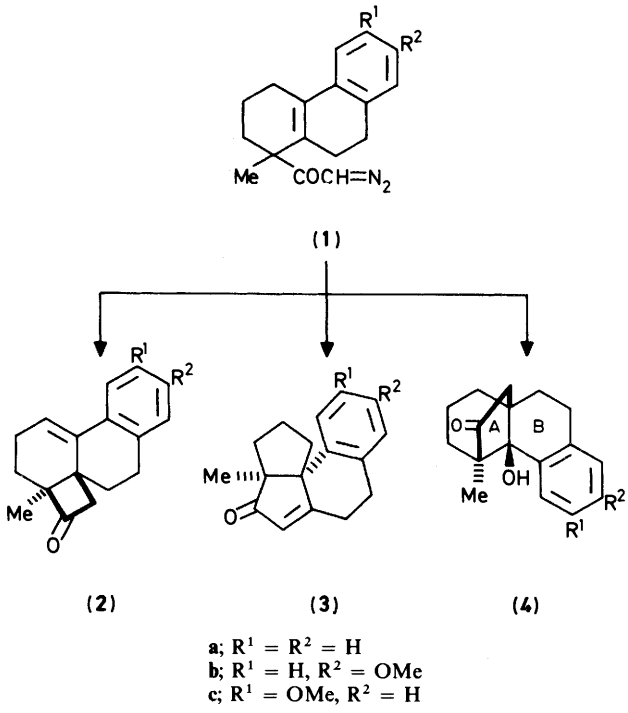
Some transformations of the octahydro-4a-hydroxy-4,10a-ethanophenanthren-12-ones (**4a—c**), derived *via* acid-catalysed alkylation–rearrangement reactions, are described. Hydrogenolysis of the hydroxycyclopentanones (**4a—c**) with lithium–ammonia proceeds with retention of configuration to give the respective bridged ketones (**6a—c**) exclusively; these have been converted into the corresponding octahydrophenanthrene-4,10a-*cis*-dicarboxylic acids (**10a—c**). Formylation–oxidation of compounds (**4a**) and (**4c**) led to the hydroxy γ-lactonic acid (**12a**) and the dihydroxy dicarboxylic acid (**16c**) respectively. The structure of compound (**12a**) has been established by *X*-ray crystallography. The α-keto γ-lactonic esters (**15a**) and (**15c**), obtained from compounds (**12a**) and (**16c**), respectively, on oxidative fragmentation led to the respective benzocyclodecenone derivatives (**19a**) and (**19c**). The *p*-methoxy ketone (**4b**) underwent a novel fragmentation reaction with ethyl formate and sodium hydride giving the hydroxymethylene ester (**21**), the structure of which has been established by *X*-ray crystallography.

Recent investigations in our laboratories have shown[2,3] that, with different reagents and reaction conditions, acid-catalysed cyclisation–rearrangement reactions of the easily accessible hexahydrophenanthrene diazoacetyl derivatives (**1a—c**) afford the respective unsaturated cyclobutanones (**2a—c**), pentaleno annelated tetralins (**3a—c**), and the bridged hydroxycyclopentanones (**4a—c**) (Scheme 1) in excellent yields. The usefulness of the cyclobutanones (**2a—c**) for stereospecific angular alkylation has been demonstrated[4-6] by their conversion into substituted octahydrophenanthrene derivatives, key intermediates in the synthesis of certain complex diterpenoids. In this paper we describe in detail some interesting transformations of the hydroxycyclopentanones (**4a—c**) involving some novel oxidative fragmentation reactions to give a number of functionalised octahydrophenanthrene and benzocyclodecenone derivatives.

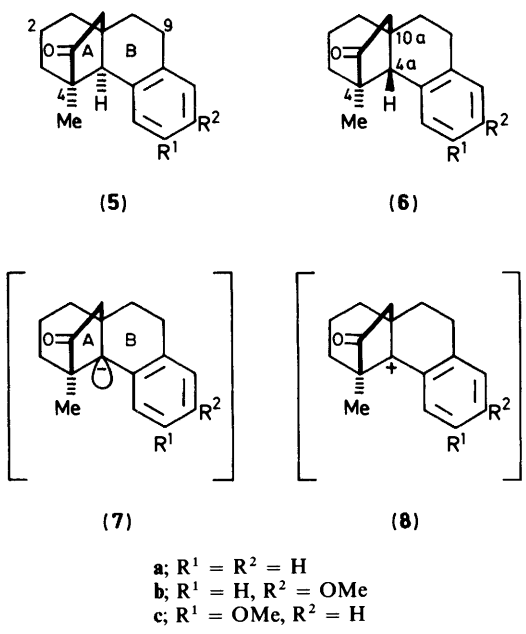


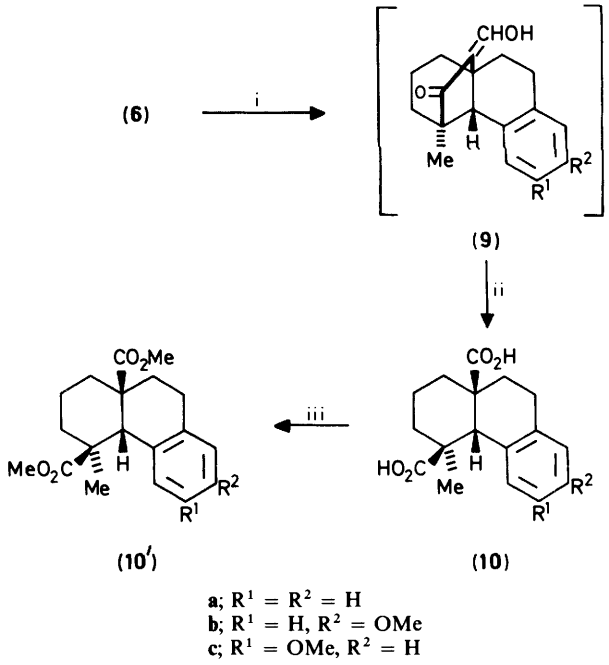
a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = OMe$
c; $R^1 = OMe$, $R^2 = H$

Scheme 1.

Results and Discussion

As reported earlier,[2] the catalytic hydrogenation of compounds (**4a—c**) over palladium–charcoal produced the respective hydrogenolysed products (**5a—c**) in excellent yields, through *inversion* of configuration at the benzylic asymmetric centre (C-4a). The stereochemistries of compounds (**5a**) and (**5b**) have been established[2] by single-crystal *X*-ray analysis. We have now found that reductive cleavage of the hydroxycyclopentanones (**4a—c**) with lithium in liquid ammonia[7] followed by oxidation with Jones reagent give exclusively the corresponding crystalline ketones (**6a—c**) in 80—90% yields, with *retention* of configuration[8] at C-4a. The i.r. and ^1H n.m.r. spectral data of these ketones are in complete agreement with the assigned structures (see Experimental section). As expected, the C-4 methyl singlet in the *cis*-A/B-ketones (**6a—c**) appears at δ 1.43 in the ^1H n.m.r. spectra, significantly downfield from the C-4 methyl singlet (δ 1.23—1.25) in the epimeric *trans*-A/B-ketones (**5a—c**), and close to those observed for the starting hydroxycyclopentanones (**4a—c**) (δ 1.46, 1.45, and 1.43 respecti-





vely[2]). As mentioned previously, the *X*-ray structure of compound (**4a**) clearly revealed[3] that the six-membered ring A in this compound has a boat conformation with the C-4 methyl group in the plane of the aromatic ring (deshielding zone). Evidently, the ketones (**6a**—**c**) have identical conformations. The complete *retention* of stereochemistry at the benzylic C-4a centre in the lithium–ammonia induced hydrogenolysis of the hydroxycyclopentanones (**4a**—**c**) is readily visualised as proceeding through protonation[7,8] of the intermediate carbanions (**7a**—**c**). It should be noted here that compounds (**4a**—**c**) also resulted from hydroxylation[2,3] of the respective carbocations (**8a**—**c**) in their formation from the diazo ketones (**1a**—**c**). In both cases the stereochemistry of the products is probably controlled by the thermodynamic stability.

With the C-4a epimeric ketones (**5a**—**c**) and (**6a**—**c**) in hand, attention was next directed to the development of the 4,10a-*cis*-dicarboxylic acid functions in the *trans*- and *cis*-octahydrophenanthrene moieties *via* a formylation–oxidation sequence.[8,9] The attempted formylation[9] of compound (**5a**) under forcing conditions with an excess of ethyl formate in the presence of sodium hydride or sodium methoxide failed to give the respective hydroxymethylene derivative. Similarly, under identical conditions compounds (**5b**) and (**5c**) were recovered unchanged. Examination of Dreiding models clearly indicates that the failure of the *trans*-A/B-ketones (**5a**—**c**) to undergo hydroxymethylation can be attributed to the large steric interactions of the C-2 and C-9 axial methylene hydrogens with the $COCH_2$ moiety. In contrast, the epimeric ketone (**6a**) reacted smoothly with ethyl formate and sodium hydride to afford the corresponding hydroxymethylene derivative (**9a**) in 90% yield. The crude product on oxidation with alkaline hydrogen peroxide (30%) afforded the crystalline diacid (**10a**) in 92% yield. In an identical sequence, the methoxy ketones (**6b**) and (**6c**) gave the respective diacids (**10b**) and (**10c**) in excellent yields *via* the intermediates (**9b**) and (**9c**). The diacids (**10a**—**c**) were further characterised through their respective dimethyl esters (**10a**—**c'**) (Scheme 2). To our knowledge, compounds (**10a**—**c**) are the first octahydrophenanthrene derivatives incorporating 4-*gem*-carboxymethyl and 10a-carboxy function.

The formylation–oxidation sequence was next extended to the hydroxycyclopentanone (**4a**) (Scheme 3). The crude hydroxymethylene ketone (**11a**), prepared from compound (**4a**) under the aforementioned conditions, on oxidation with

Scheme 2. *Reagents*: i, NaH, HCO_2Et, C_6H_6; ii, aq. NaOH, H_2O_2 (30%); iii, CH_2N_2, Et_2O

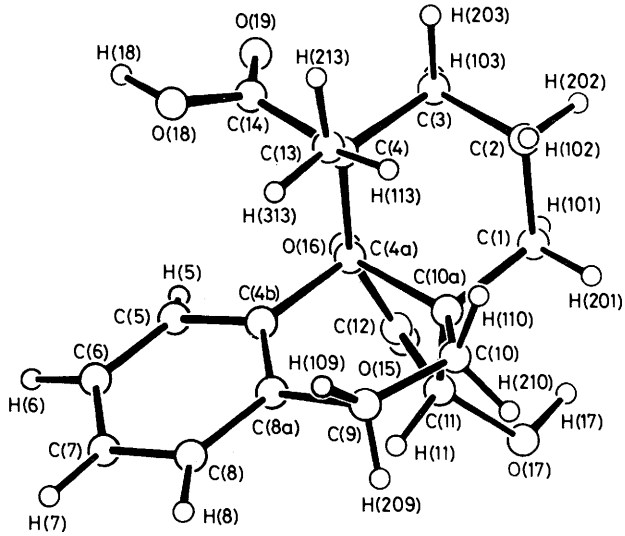


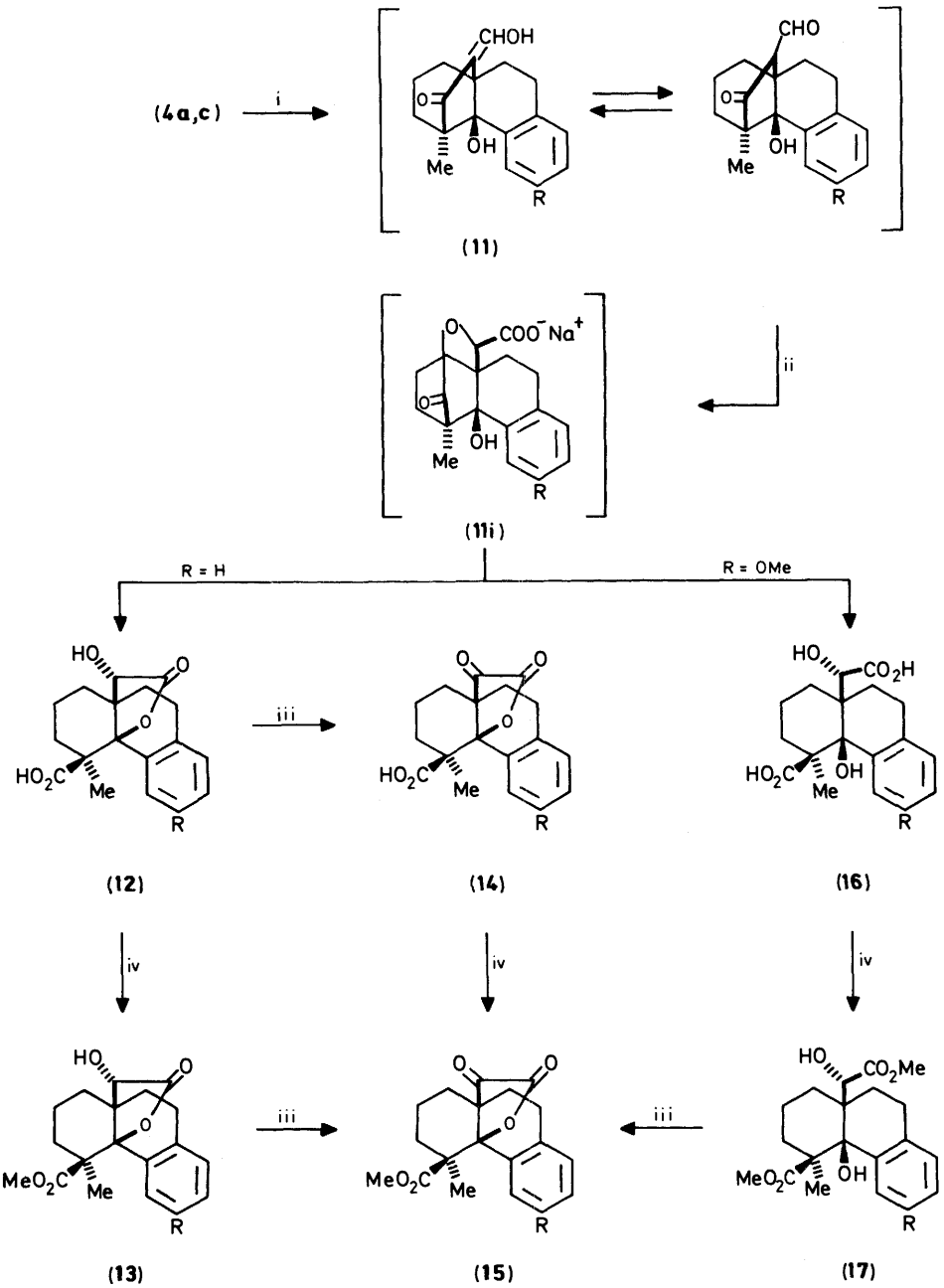
Figure 1. Perspective view of the hydroxy γ-lactonic acid (**12a**) showing the crystallographic numbering scheme used

alkaline hydrogen peroxide (30%) afforded the hydroxy γ-lactone acid (**12a**) (m.p. 223—225 °C) in 69% overall yield. The structure of this compound was initially assigned from the spectral data of the corresponding methyl ester (**13a**) (diazomethane). The i.r. spectrum of compound (**13a**) exhibited strong absorptions at 3 460, 1 760, and 1 720 cm^{-1} consistent with the presence of hydroxy, γ-lactone, and ester chromophores. Its ^1H n.m.r. spectrum showed a methyl singlet at δ 1.0, a secondary OH proton signal at δ 3.33 (exchangeable with D_2O), C*H*OH singlet at δ 3.97, and a CO_2CH_3 singlet at δ 3.73. The mass spectrum of the ester (**13a**) showed the molecular ion peak at *m/z* 330 (M^+, 12.5%) and two strong peaks at *m/z* 302 (M − 28, 33%), and *m/z* 274 (M − 56, 100%) corresponding to the loss of one and two molecules of carbon monoxide

respectively. The presence of a secondary OH group was further confirmed by oxidation with Jones reagent of the acid (**12a**) and the methyl ester (**13a**) to give the respective α-keto-lactones (**14a**) and (**15a**) in excellent yields. Finally, the complete structure and stereochemistry of compound (**12a**) has been determined by an *X*-ray crystal structure analysis, and a perspective drawing of the final structure is shown in Figure 1.

To ascertain whether the above sequence is generally applicable, the methoxy derivative (**4c**) was subjected to an identical series of reactions (Scheme 3). The crude hydroxymethylene ketone (**11c**) on oxidation with alkaline hydrogen peroxide gave the dihydroxy dicarboxylic acid (**16c**) (m.p. 232—233 °C) in good yield. Surprisingly, unlike the demethoxy analogue, the diacid (**16c**) did not lactonise during its isolation or even on treatment with dilute HCl or H_2SO_4. The assigned structure of this compound was further supported by the spectral data (see Experimental section) of the corresponding dimethyl ester (**17c**). The stereochemistry of compound (**16c**) has been assigned by analogy with that of the lactonic acid (**12a**) which could reasonably be formed *via* a similar intermediate (**16a**). (We have so far been unable to isolate this intermediate.) The reason for the reluctance of compound (**16c**) to undergo lactonisation is not clear. However, oxidation of the dihydroxy diester (**17c**) with Jones reagent gave the corresponding α-keto lactonic ester (**15c**) in excellent yield.

The formation of the hydroxy γ-lactonic acid (**12a**) and the dihydroxy dicarboxylic acid (**16c**) from the hydroxymethylene derivatives (**11a**) and (**11c**) [derived from the hydroxycyclo-

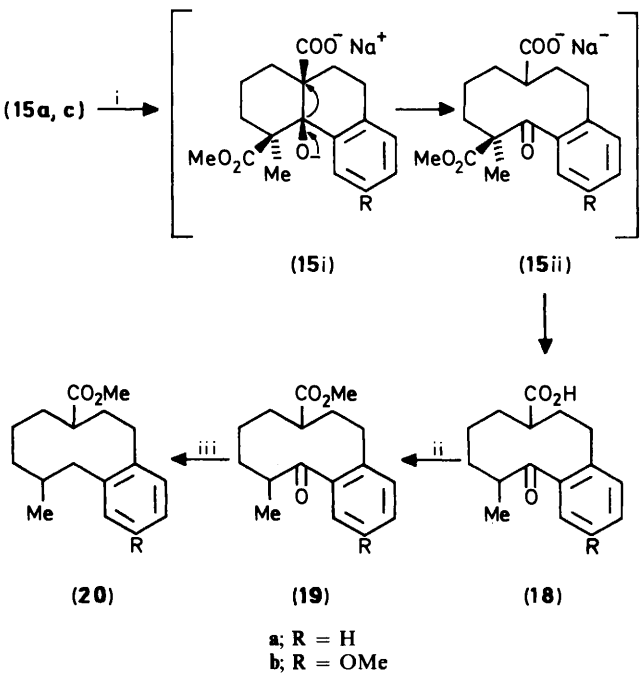


Scheme 3. *Reagents*: i, NaH, HCO_2Et, C_6H_6; ii, NaOH (10%), H_2O_2 (30%), HCl; iii, Jones reagent; iv, CH_2N_2–Et_2O

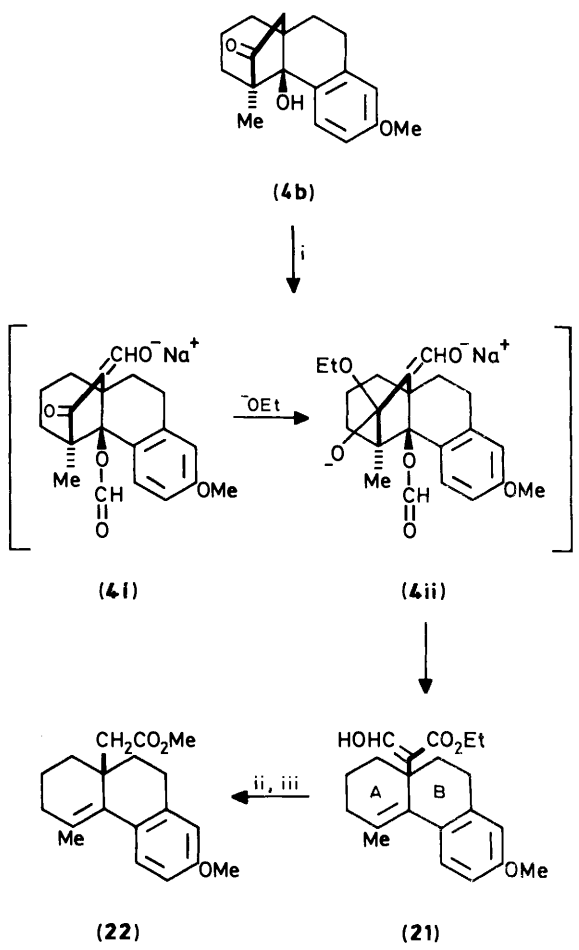
pentanones (**4a**) and (**4c**) respectively], with alkaline hydrogen peroxide, contrast with the oxidations of the hydroxymethylene ketones (**9a**—**c**) [from the cyclopentanones (**6a**—**c**), or similar substrates [6,9]] which give rise to the corresponding dicarboxylic acids (**10a**—**c**) with the loss of a carbon residue. It is known that an aldehyde function may undergo oxidation with alkaline hydrogen peroxide to give the respective acid.[10] Also the same reagent can result in Baeyer–Villiger oxidation [3,11] in the case of strained ketones. It is possible that owing to the presence of the neighbouring hydroxy group,[12] the oxidations of compounds (**11c**) and (**11a**) with alkaline hydrogen peroxide follow a similar course of reactions leading to the lactonic acid intermediate (**11i**); this then undergoes hydrolytic ring opening to give the dihydroxy diacid (**16c**), or the γ-lactonic acid (**12a**) by subsequent *trans*-lactonisation (Scheme 3).

In order to bring about ring fragmentation, the α-keto lactone ester (**15a**) was subjected to oxidative degradation with alkaline hydrogen peroxide (30%) in aqueous ethanol or t-butyl alcohol. In both cases only intractable neutral and acidic product mixtures were isolated. Finally, alkaline hydrogen peroxide oxidation of compound (**15a**) in a two-phase system using methylene dichloride gave the acid (**18a**) as a viscous oil in 73% yield; it was characterised by its i.r. spectrum [ν_{max}(neat) 1 700, 1 680, and 1 600 cm^{-1}] (Scheme 4). This acid was converted into the corresponding methyl ester (**19a**) with diazomethane, which showed two strong C=O absorptions in the i.r. spectrum at 1 735 and 1 680 cm^{-1} corresponding to an ester and an aromatic conjugated ketonic C=O group. The u.v. spectrum exhibited absorptions at 247 (log ε 4.19) and 290 nm (3.38), consistent with the assigned structure. The ^{1}H n.m.r. spectrum of compound (**19a**) showed signals at δ 1.17 (d, *J* 7 Hz, Me), 2.77—3.10 (m, 2 benzylic H), and 3.63 (s, CO_2CH_3), and a deshielded (due to the C=O group) *ortho* aromatic proton at δ 7.83—8.07 (m). The expected molecular formula was confirmed by both the mass spectrum and the elemental analysis. The aromatic conjugated C=O group in the ester (**19a**) underwent slow hydrogenolysis in the presence of palladium–charcoal (10%) in methanol containing a catalytic amount of perchloric acid (70%) to afford the ester (**20a**), which was characterised by the i.r. and ^{1}H n.m.r. spectra. Following an identical sequence (Scheme 4), the methoxy α-keto γ-lactonic ester (**15c**) was oxidised to afford an acidic product which was directly esterified with diazomethane. The crude ester on separation by p.l.c., afforded the desired macrocyclic keto ester (**19c**) as the only isolable product in low yield. The spectral data of compound (**19c**) are in complete agreement with the assigned structure (see Experimental section). The observed fragmentation of compounds (**15a**) and (**15c**) to the benzocyclodecenone carboxylic acids (**18a**) and (**18c**) can be rationalised through the respective intermediate anion (**15i**) (Scheme 4), which results from the alkaline peroxide induced cleavage [10] of the ⩾CO–C(O) bond. This intermediate undergoes a retro aldol type reaction [13] to give the β-keto ester (or acid) intermediate (**15ii**), subsequent hydrolytic decarboxylation of which leads to the respective keto acids (**18a**) and (**18c**) (Scheme 4).

In contrast to the demethoxy- and the 6-methoxy-hydroxycyclopentanones (**4a**) and (**4c**) respectively, the 7-methoxyketone (**4b**) on formylation [9] with ethyl formate in the presence of sodium hydride (Scheme 5) underwent fragmentation to give the crystalline hydroxymethylene ethyl ester (**21**) in 75% yield. The spectral data (see Experimental section) of this compound are in complete agreement with the assigned structure. This compound on hydrolysis with aqueous potassium hydroxide gave the respective deformylated acid which was directly esterified with diazomethane to the respective methyl ester (**22**) (characterised by i.r. and ^{1}H n.m.r. spectral data). Finally, the



Scheme 4. *Reagents*: i, CH_2Cl_2, NaOH (10%), H_2O_2 (30%); ii, CH_2N_2–Et_2O; iii, Pd–C-10%, MeOH, $HClO_4$ (70%)



Scheme 5. *Reagents*: i, NaH, HCO_2Et, C_6H_6; ii, KOH, EtOH; iii, CH_2N_2–Et_2O

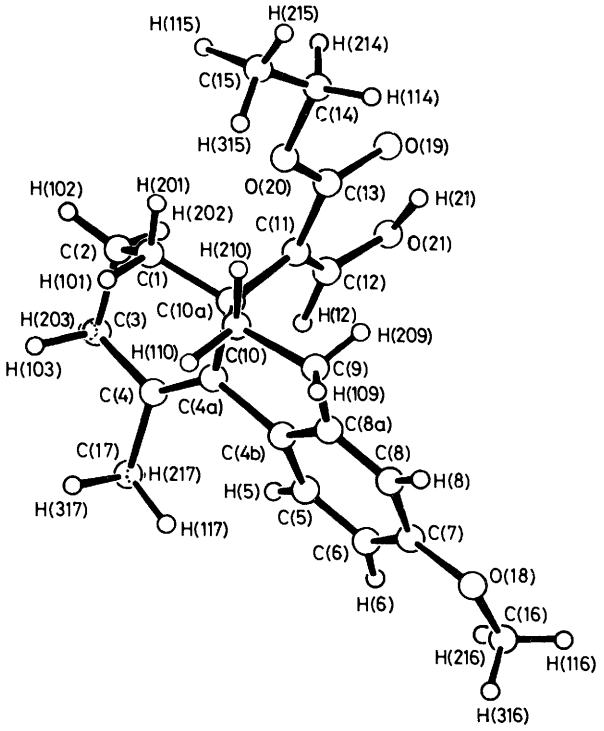


Figure 2. Perspective view of the hydroxymethylene ester (**21**) showing the crystallographic numbering scheme used

complete structure of compound (**21**) has been established by an *X*-ray crystal structure analysis, and a perspective drawing of the final conclave is shown in Figure 2. It should be noted that rings A and B in compound (**21**) have half-sofa and half-chair conformations, respectively. There is an intramolecular hydrogen bond between the ester C=O and the hydroxymethylene OH groups.

It is evident that ethyl formate plays an important role in the fragmentation of the hydroxycyclopentanone (**4b**) as the latter compound can be recovered on treatment with refluxing sodium hydride in benzene containing ethanol or sodium ethoxide in ethanol. Possibly, *trans*-esterification of compound (**4b**) during the formylation reaction leads to the formate (**4i**), which undergoes a *syn*-periplanar fragmentation[14] through the intermediate (**4ii**) (Scheme 5). Certainly, the presence of a *p*-methoxyaryl residue in compound (**4b**) would facilitate the fragmentation *via* intermediates (**4i**) and (**4ii**). However, there are other possible paths for the fragmentation of compound (**4b**), and at this stage no definite mechanism for this interesting fragmentation reaction can be proposed.

In conclusion, the present work provides efficient synthetic routes to some angularly functionalised octahydrophenanthrenes involving a few interesting fragmentation reactions of the easily accessible intermediates from certain β,γ-unsaturated diazomethyl ketones. The facile formation of benzocyclodecenone derivatives[15] has opened up new synthetic possibilities for some macrocyclic natural products.

Experimental

The compounds described are all racemates. M.p.s and b.p.s are not corrected. 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 Beckman DU or a Shimatzu UV Vis 210A spectrometer for solutions in 95% ethanol Unless otherwise stated, ^{1}H n.m.r. spectra were recorded at 60 MHz on a Varian T-60A spectrometer in $CDCl_3$ solutions with $SiMe_4$ as internal standard. 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-ionisation detector and a 20 × $\frac{1}{8}$ in 10% UCW column, at 190 °C with N_2 as the carrier gas. Elemental analyses were performed by P. P. Bhattacharyya of this laboratory. Column chromatography was performed on neutral alumina (Brockman Grade I). Petroleum and light petroleum refer to fractions of b.p. 60—80 and 40—60 °C respectively. Ether refers to diethyl ether.

Hydrogenolysis of the 4aβ-*Hydroxycyclopentanones* (**4a—c**) *with* Li–NH_3.—(±)-4α-*Methyl*-1,2,3,4,4aβ,9,10,10a-*octahydro*-4β,10aβ-*ethanophenanthren*-12-*one* (**6a**). To a magnetically stirred solution of the 4aβ-hydroxy compound (**4a**)[2,3] (500 mg, 1.95 mmol) in dry ether (15 ml), and anhydrous liquid NH_3 (250 ml), distilled over Na, was added freshly scraped Li wire (294 mg, 42 mg-atom) in small portions (*ca.* 3 min). Stirring was continued for another 5 min, an excess of powdered NH_4Cl was added, and the NH_3 was allowed to evaporate. The residue was carefully acidified with 6M-HCl, and extracted with ether. After removal of the dried (Na_2SO_4) solvent, the crude viscous gum (450 mg) (ν_{max} 3 460, 1 730, and 1 600 cm^{-1}) was dissolved in acetone (5 ml) and oxidised with Jones reagent[16] at 10—15 °C until the colour of the reagent persisted for 10 min; the mixture was then worked up. The crude product (homogeneous in g.l.c.) was chromatographed on silica gel (10 g). Elution with light petroleum afforded the *cyclopentanone* (**6a**) (420 mg, 90%), m.p. 90—91 °C (light petroleum) (Found: C, 84.9; H, 8.4. $C_{17}H_{20}O$ requires C, 84.95; H, 8.39%), ν_{max} 2 920, 2 845, 1 738, 1 485, 1 450, 1 405, 1 370, 1 080, 765, and 750 cm^{-1}; δ 1.43 (s, 3 H, CH_3), 1.50—1.98 (m, 8 H), 2.04 (δ_A) and 2.35 (δ_B) (AB_q, *J* 18 Hz, 2 H, $COCH_2$), 2.66—3.13 (m, 3 H, ArCH_2 and Ar*CH*), and 6.90—7.50 (m, 4 H, ArH).

(±)-7-*Methoxy*-4α-*methyl*-1,2,3,4,4aβ,9,10,10a-*octahydro*-4β,10aβ-*ethanophenanthren*-12-*one* (**6b**) Reduction of the 4aβ-hydroxy compound (**4b**)[2] (500 mg, 1.75 mmol) in ether (15 ml) with Li wire (294 mg, 42 mg-atom) in anhydrous liquid NH_3 (200 ml), as described for compound (**4a**), followed by oxidation with Jones reagent afforded a light yellow viscous material (homogeneous in g.l.c.) which was chromatographed on silica gel (10 g). Elution with light petroleum afforded the *cyclopentanone* (**6b**) (420 mg, 89%), m.p. 131—132 °C (light petroleum) (Found: C, 79.8; H, 8.15. $C_{18}H_{22}O_2$ requires C, 79.96; H, 8.2%, ν_{max} 2 930, 2 860, 1 738, 1 610, 1 495, 1 250, 1 100, 1 035, 890, and 795 cm^{-1}; δ 1.43 (s, 3 H, CH_3), 1.5—2.0 (m, 8 H), 2.04 (δ_A) and 2.35 (δ_B) (AB_q, *J* 18 Hz, 2 H, $COCH_2$), 2.6—3.08 (m, 3 H, ArCH_2 and Ar*CH*), 3.76 (s, 3 H, ArOCH_3), and 6.5—7.33 (m, 3 H, ArH).

(±)-6-*Methoxy*-4α-*methyl*-1,2,3,4,4aβ,9,10,10a-*octahydro*-4β,10aβ-*ethanophenanthren*-12-*one* (**6c**). Reduction of compound (**4c**)[2] (500 mg, 1.75 mmol) in ether (20 ml) and anhydrous liquid NH_3 (200 ml) with Li wire (294 mg, 42 mg-atom) as described for compound (**4a**), followed by oxidation with Jones reagent afforded a semi-solid mass (homogeneous in g.l.c.), which was chromatographed on silica gel (10 g). Elution with light petroleum afforded the *cyclopentanone* (**6c**) (378 mg, 80%), m.p. 112 °C (light petroleum) (Found: C, 79.6; H, 8.1. $C_{18}H_{22}O_2$ requires C, 79.96; H, 8.2%), $\nu_{max.}$ 2 930, 2 860, 1 735, 1 606, 1 500, 1 470, 1 220, 1 165, 1 085, 1 040, 945, and 920 cm^{-1}; δ (100 MHz) 1.43 (s, 3 H, CH_3), 1.48—1.96 (m, 8 H), 2.08 (δ_A) and 2.42 (δ_B) (AB_q, *J* 18 Hz, 2 H, $COCH_2$), 2.72—2.96 (m, 3 H, ArCH_2 and Ar*CH*), 3.76 (s, 3 H, ArOCH_3), and 6.64—7.08 (m, 3 H, ArH).

Hydroxymethylation followed by Oxidation of the Cyclopentanones (**6a—c**).—(±)-4α-*Methyl*-1,2,3,4,4aβ,9,10,10a-*octahydrophenanthrene*-4β,10aβ-*dicarboxylic acid* (**10a**). To a

magnetically stirred suspension of NaH (350 mg, 14.6 mmol) in dry benzene (5 ml), cooled in an ice-bath under N_2, a solution of the ketone (**6a**) (250 mg, 1.04 mmol) in dry benzene (5 ml) was added, followed by a drop of dry MeOH. Stirring was continued at the same temperature for 1 h, ethyl formate (1.25 ml, 15.5 mmol) was then added dropwise to the cold stirred mixture, stirring was continued for a further 2 h and the mixture then left overnight at room temperature. The excess of NaH was decomposed by dropwise addition of MeOH followed by cold water. The neutral material was extracted with ether to afford a small amount of a brown gum which was not characterised. The basic aqueous part and the washings were chilled together and acidified with 6M-HCl. The organic material was extracted with ether to afford the hydroxymethylene ketone (**9a**) (250 mg, 90%), as a brown gum, ν_{max} 1 665 and 1 605 cm^{-1}, which responded to the $FeCl_3$ colour reaction. This product, without further purification, was dissolved in aqueous NaOH (20 ml, 10%) and maintained at 10—15 °C (bath temperature). To it was added dropwise, with stirring, aqueous H_2O_2 (10 ml, 30%) during 20—25 min and stirring was continued for 1 h. A second aliquot of aqueous NaOH (20 ml, 10%) was added in one portion, followed by the dropwise addition of H_2O_2 (10 ml, 30%). The mixture was stirred for another 2 h at room temperature and then left overnight. The solution was diluted with water, acidified with 6M-HCl, and extracted with ethyl acetate. The ethyl acetate extract was washed with water and dried (Na_2SO_4). Removal of the solvent afforded the *diacid* (**10a**) [250 mg; 83% based on (**6a**)], m.p. 233—234 °C (decomp.) (ethyl acetate) (Found: C, 70.75; H, 7.1. $C_{17}H_{20}O_4$ requires C, 70.81; H, 6.99%); ν_{max} 2 940, 2 860, 1 690, and 1 600 cm^{-1}).

The dicarboxylic acid (**10a**) (100 mg, 0.35 mmol) in ether (20 ml) was esterified with an excess of CH_2N_2 in ether, which was purified by filtration (in petroleum) through a short-packed column of alumina, to afford (±)-*dimethyl* 4α-*methyl*-1,2,3,4,-4aβ,9,10,10a-*octahydrophenanthrene*-4β,10aβ-*dicarboxylate* (**10a'**) (90 mg, 82%) as a colourless thick liquid (homogeneous in g.l.c.); ν_{max} 2 950, 2 860, 1 725, 1 600, 1 490, 1 450, 1 430, 1 380, 1 260, 1 110, 1 050, 790, and 765 cm^{-1}; λ_{max} 252, 267, and 274 (log ε 2.89, 2.82, and 2.75); δ(CCl_4) 0.93 (s, 3 H, CH_3), 1.37—2.37, (m, 8 H), 2.70—3.07 (m, 2 H, ArCH_2), 3.47 (s, 3 H, CO_2CH_3), 3.70 (s, 3 H, CO_2CH_3), 3.90 (br s, 1 H, ArC*H*), and 6.57—7.13 (m, 4 H, ArH).

(±)-7-*Methoxy*-4α-*methyl*-1,2,3,4,4aβ,9,10,10a-*octahydrophenanthrene*-4β,10aβ-*dicarboxylic acid* (**10b**). Following the procedure described for compound (**6a**), the ketone (**6b**) (250 mg, 0.93 mmol) was converted into its hydroxymethylene derivative (**9b**) (230 mg, 83%); $\nu_{max.}$ ($CHCl_3$) 2920, 1680, and 1605 cm^{-1}. This crude product (230 mg) gave on oxidation with alkaline H_2O_2 (30%) as described above the crude diacid as a pale yellow solid, which was purified by chromatography on silica gel, using 30% ether–petroleum as eluant, to afford the pure *diacid* (**10b**) [220 mg, 75%, based on (**6b**)] m.p. 210 °C (ether–light petroleum) (Found: C, 67.75; H, 7.15. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.97%); ν_{max} 2 950, 2 870, 1 690, and 1 605 cm^{-1}.

The dicarboxylic acid (**10b**) (100 mg, 0.314 mmol) in ether (15 ml) was esterified with CH_2N_2 in ether and the product was purified by filtration (in petroleum) through a short-packed column of alumina to give (±)-*dimethyl* 7-*methoxy*-4α-*methyl*-1,2,3,4,4aβ,9,10,10a-*octahydrophenanthrene*-4β,10aβ-*dicarboxylate* (**10b'**) (97 mg, 89%) as a colourless thick liquid (homogeneous in g.l.c.); ν_{max} 2 950, 2 860, 1 725, 1 605, 1 500, 1 460, 1 430, 1 235, 1 165, 1 110, and 1 040 cm^{-1}; λ_{max} 280 nm (log ε 3.72); δ 0.94 (s, 3 H, CH_3), 1.52—2.4 (m, 8 H), 2.72—3.0 (m, 2 H, ArCH_2), 3.46 (s, 3 H, CO_2CH_3), 3.72 (s, 6 H, CO_2CH_3 and ArOCH_3), 3.8 (br s, 1 H, ArC*H*), and 6.26—6.73 (m, 3 H, ArH).

(±)-6-*Methoxy*-4α-*methyl*-1,2,3,4,4aβ,9,10,10a-*octahydrophenanthrene*-4β,10aβ-*dicarboxylic acid* (**10c**). Following the procedure described for compound (**6a**), the ketone (**6c**) (240 mg, 0.89 mmol) was converted into its hydroxymethylene derivative (**9c**) (236 mg, 89%), obtained as a thick brown liquid; ν_{max} 1 660 and 1 600 cm^{-1}. This crude product, on oxidation with alkaline H_2O_2 (30%) as described for the analogue (**9a**), gave the *diacid* (**10c**) (231 mg, 82% overall yield), m.p. 220—221 °C (decomp.) (ethyl acetate) (Found: C, 67.75; H, 7.15. $C_{18}H_{22}O_5$ requires C, 67.91; H, 6.97%); ν_{max} 2 940, 2 860, 1 695, and 1 605 cm^{-1}.

The dicarboxylic acid (**10c**) (100 mg, 0.314 mmol) was esterified with CH_2N_2 in ether and the crude product was purified by filtration (in petroleum) through a short-packed column of alumina to afford (±)-*dimethyl* 7-*methoxy*-4α-*methyl*-1,2,3,4,4aβ,9,10,10a-*octahydrophenanthrene*-4β,10aβ-*dicarboxylate* (**10c'**) (98 mg, 90%) as a colourless oil (homogeneous in g.l.c.); ν_{max} 2 950, 2 860, 1 725, 1 610, 1 500, 1 460, 1 430, 1 240, 1 135, 1 110, and 1 040 cm^{-1}; λ_{max} 224 and 280 nm (log ε 4.07 and 3.54); δ 0.96 (s, 3 H, CH_3), 1.25—2.4 (m, 8 H), 2.72—3.0 (m, 2 H, ArCH_2), 3.50 (s, 3 H, CO_2CH_3), 3.68 and 3.70 (s × 2, 6 H, CO_2CH_3 and ArOCH_3), 4.0 (br s, 1 H, ArC*H*), and 6.36—7.04 (m, 3 H, ArH).

Formylation–Oxidation of the Hydroxycyclopentanone (**4a**) *to give* (4aRS,4SR,10aSR,11RS)-4a-*Hydroxy*-4-*carboxy*-4-*methyl*-1,2,3,4,4a,9,10,10a-*octahydrophenanthren*-10a-*yl*-*(hydroxy)acetic Acid* 4a,10a-*Lactone* (**12a**).—Following the procedure described for compound (**6a**), the hydroxy ketone (**4a**) (250 mg, 0.98 mmol in dry benzene (5 ml) was converted into its hydroxymethylene derivative (**11a**) by reaction with NaH (500 mg, 21 mmol) in dry benzene (5 ml) followed by the addition of ethyl formate (2 ml, 24.7 mmol). The hydroxymethylene derivative (**11a**) (265 mg, 96%); ν_{max} 1 710, 1 660, and 1 600 cm^{-1}, was obtained as a brown gummy mass. The crude product (260 mg, 0.91 mmol), dissolved in aqueous NaOH (30 ml, 10%), was oxidised by the addition of aqueous H_2O_2 (10 ml, 30%) at 10—15 °C followed by the addition of a second portion of aqueous NaOH (20 ml, 10%) and H_2O_2 (3 ml, 30%) after 2 h at room temperature. The mixture was stirred at room temperature for an additional 3 h, left overnight, then diluted with water and worked up with ether. The small amount of residue left after evaporation of the ether was discarded.

The combined basic aqueous part and the washings were chilled and acidified with 6M-HCl and the precipitated solid was extracted with CH_2Cl_2. The organic layer was washed with brine and dried (Na_2SO_4). Removal of the solvent gave a pale yellow solid which on recrystallisation from acetone gave the *hydroxy lactonic acid* (**12a**) (200 mg, 69%), m.p. 223—225 °C (decomp.) (Found: C, 68.2; H, 6.6. $C_{18}H_{20}O_5$ requires C, 68.34; H, 6.37%); ν_{max} 3 380, 3 245, 1 765, 1 705, 1 450, 1 330, 1 215, 1 155, 1 130, 985, and 760 cm^{-1}.

Esterification of the Hydroxy Lactonic Acid (**12a**) *to give the Methyl Ester* (**13a**).—A solution of compound (**12a**) (150 mg, 0.47 mmol) in acetone (5 ml) was esterified with an excess of CH_2N_2 in ether. Removal of the solvent afforded the *ester* (**13a**) (150 mg, 96%) as a pale yellow solid, m.p. 175—180 °C. The analytical sample was prepared by recrystallisation from ethyl acetate–petroleum (2:1), m.p. 180 °C (Found: C, 69.1; H, 6.6. $C_{19}H_{22}O_5$ requires C, 69.07; H, 6.71%); ν_{max} 3 460, 1 760, 1 720, 1 450, 1 255, 1 195, 1 150, 1 120, 1 100, 1 020, 985, 850, and 725 cm^{-1}; δ 1.0 (s, 3 H, CH_3), 1.33—2.33 (m, 8 H), 2.88 (br d, *J* 7 Hz, 2 H, ArCH_2), 3.33 (s, 1 H, OH, exchangeable with D_2O), 3.73 (s, 3 H, CO_2CH_3), 3.97 (s, 1 H, C*H*OH), and 7.1 (br s, 4 H, ArH); *m/z* (relative intensity) 330 (M^+, 12.5), 302 (33), 274 (100), 252 (17), 224 (34), and 197 (58).

Oxidation of the Hydroxy γ-Lactonic Methyl Ester (**13a**) *to give the α-Keto γ-Lactonic Ester* (**15a**).—To a magnetically stirred solution of the ester (**13a**) (150 mg, 0.45 mmol) in acetone (5 ml) at room temperature, Jones reagent was added dropwise until the brown colour of the reagent persisted. The solution was stirred for an additional 1 h, the excess of reagent was decomposed by the addition of isopropyl alcohol, and the mixture diluted and extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated to afford the *ester* (**15a**) (140 mg, 94%), m.p. 153 °C (ethyl acetate–petroleum) (Found: C, 69.3; H, 6.2. $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.14%); ν_{max} 2 950, 1 795, 1 725, 1 605, 1 125, 1 080, 1 050, and 980 cm^{-1}); δ 1.1 (s, 3 H, CH_3), 1.33—2.4 (m, 8 H), 2.93—3.16 (m, 2 H, $ArCH_2$), 3.8 (s, 3 H, CO_2CH_3), and 7.13 (s, 4 H, ArH).

Oxidation of the Hydroxy γ-Lactonic Acid (**12a**) *to give the α-Keto γ-Lactonic Acid* (**14a**), *and the Conversion of the Latter Compound into the Methyl Ester* (**15a**).—The hydroxy γ-lactonic acid (**12a**) (150 mg, 0.47 mmol) in acetone (5 ml) was oxidised with Jones reagent as described for the ester (**13a**). The α-keto lactonic acid (**14a**) (140 mg, 94%), m.p. 198—200 °C (decomp.) was obtained as a colourless solid; ν_{max} 2 945, 1 790, 1 770, 1 700, 1 295, 1 200, 1 135, 1 080, and 930 cm^{-1}.

The acid (**14a**) (75 mg, 0.24 mmol) in acetone (3 ml) was esterified with CH_2N_2 in ether to afford the ester (**15a**) (75 mg, 96%), m.p. 153 °C alone or in admixture with the sample described above.

Formylation–Oxidation of the Hydroxycyclopentanone (**4c**) *to give the Dihydroxy Dicarboxylic Acid* (**16c**).—A solution of compound (**4c**) (200 mg, 0.7 mmol) in benzene (5 ml) was formylated with NaH (200 mg, 8.33 mmol) and ethyl formate (2 ml, 24.7 mmol) as described for the demethoxy analogue (**4a**) to afford the formylated product (**11c**) (200 mg, 91%) as a thick brown liquid [ν_{max}($CHCl_3$) 1 710, 1 680, 1 600, and 1 570 cm^{-1}]. The crude product was oxidised with alkaline H_2O_2 (30%) as described for compound (**11a**) to afford the *dihydroxy dicarboxylic acid* (**16c**) (202 mg, 87%) as a brown solid, m.p. 230—233 °C, which was recrystallised from ethyl acetate to give the analytically pure sample, m.p. 232—233 °C (decomp.) (Found: C, 62.5; H, 6.6. $C_{19}H_{24}O_7$ requires C, 62.62; H, 6.64%); ν_{max} 3 430, 2 960, 2 940, 1 710, 1 690, 1 610, 1 570, 1 490, 1 370, 1 285, 1 240, 1 040, 975, and 820 cm^{-1}.

Esterification of the Dihydroxy Diacid (**16c**) *to the Dimethyl Ester* (**17c**).—The diacid (**16c**) (500 mg, 1.37 mmol) in acetone (10 ml) was esterified with an excess of CH_2N_2 in ether. The crude product was chromatographed on alumina and eluted with ether–petroleum to afford the *diester* (**17c**) (500 mg, 93%), m.p. 167 °C as a colourless solid (Found: C, 64.2; H, 7.1. $C_{21}H_{28}O_7$ requires C, 64.27; H, 7.19%); ν_{max} 3 435, 2 960, 2 930, 1 725, 1 600, 1 585, 1 460, 1 350, 1 280, 1 030, 960, and 830 cm^{-1}; δ 1.08 (s, 3 H, CH_3), 1.2—3.0 (m, 13 H, 2 O*H* signals exchangeable with D_2O), 3.53 (s, 3 H, CO_2CH_3), 3.63 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, $ArOCH_3$), and 6.7—7.03 (m, 3 H, ArH).

Oxidation of the Dihydroxy Diester (**17c**) *to give the α-Keto γ-Lactonic Ester* (**15c**).—A solution of compound (**17c**) (390 mg, 1 mmol) in acetone (10 ml) was oxidised with Jones reagent as described for the hydroxy γ-lactonic ester (**13c**) to give the *α-keto γ-lactonic ester* (**15c**) (330 mg, 97%), m.p. 176—177 °C (ether–petroleum) (Found: C, 66.85; H, 6.3. $C_{20}H_{22}O_6$ requires C, 67.02; H, 6.19%); ν_{max} 2 940, 2 840, 1 795, 1 720, 1 610, 1 575, 1 500, 1 465, 1 380, 1 290, 1 270, 1 220, 1 190, 1 050, 930, and 875 cm^{-1}; δ 1.13 (s, 3 H, CH_3), 1.23—2.93 (m, 10 H), 3.75 and 3.83 (s × 2, 6 H, CO_2CH_3 and $ArOCH_3$), and 6.63—7.1 (m, 3 H, ArH).

Transformation of the α-Keto γ-Lactonic Ester (**15a**) *to* 10-*Methoxycarbonyl-6-methyl-7,8,9,10,11,12-hexahydrobenzocyclodecen-5(6H)-one* (**19a**).—To a magnetically stirred solution of compound (**15a**) (325 mg, 0.99 mmol) in CH_2Cl_2 (25 ml) at 10—15 °C, aqueous NaOH (25 ml, 10%) was added followed by aqueous H_2O_2 (10 ml, 30%). After 1 h, second portions of aqueous NaOH (25 ml, 10%) and aqueous H_2O_2 (10 ml, 30%) were added. The mixture was stirred for an additional 3 h and worked up as described for compound (**9a**) to afford a gummy neutral material (*ca.* 25 mg) which was not characterised further. The product isolated by acidification of the basic aqueous part with 6M-HCl and extraction with ether gave the keto acid (**18a**) (190 mg, 74%) as a thick colourless oil ($\nu_{max.}$ 2 980, 2 920, 1 700, 1 680, and 1 600 cm^{-1}). This keto acid (**18a**) (130 mg, 0.5 mmol) in ether (5 ml) was esterified with CH_2N_2 in ether and the crude product was purified by filtration (in petroleum) through a short-packed alumina column to afford the keto ester (**19a**) (125 mg, 91%) as a colourless oil (Found: C, 74.6; H, 8.35. $C_{17}H_{22}O_3$ requires C, 74.42; H, 8.08%); $\nu_{max.}$ 2 930, 2 860, 1 735, 1 680, 1 600, 1 510, 1 155, 1 120, 790, and 750 cm^{-1}; $\lambda_{max.}$ 247 and 290 nm (log ε 4.19 and 3.38); δ (CCl_4) 1.13 (d, *J* 7 Hz, 3 H, CH_3), 1.37—2.57 (m, 10 H), 2.77—3.1 (m, 2 H, $ArCH_2$), 3.63 (s, 3 H, CO_2CH_3), 7.0—8.0 (m, 3 H, ArH), and 7.83—8.07 (m, 1 H, *o*-COArH); *m/z* (relative intensity) 274 (M^+, 5), 241 (7), 240 (6), 213 (4), 192 (7), 156 (13), 144 (22), 143 (100), 128 (16), 113 (12), 90 (13), 89 (20), and 88 (8).

Transformation of Compound (**15c**) *to* 3-*Methoxy*-10-*methoxycarbonyl-6-methyl-7,8,9,10,11,12-hexahydrobenzocyclodecen-5(6H)-one* (**19c**).—The α-keto γ-lactonic ester (**15c**) (180 mg, 0.5 mmol) in CH_2Cl_2 (10 ml) containing aqueous NaOH (15 ml × 2, 10%) was oxidised with aqueous H_2O_2 (10 ml × 2, 30%) as described for compound (**15a**). The crude keto acid (**18c**) (ν_{max} 1 700, 1 680, and 1 600 cm^{-1}) was esterified with CH_2N_2 in ether and purified by preparative thin layer chromatography on silica gel using ethyl acetate–petroleum (2:3) to afford the *keto ester* (**19c**) (23 mg, 14%) as a colourless thick liquid (Found: C, 71.0; H, 8.2. $C_{18}H_{24}O_4$ requires C, 71.02; H, 7.95%); ν_{max} 2 940, 2 860, 1 730, 1 680, 1 610, 1 500, 1 460, 1 430, 1 270, 1 250, 1 200, and 1 170 cm^{-1}; λ_{max} 250 and 295 nm (log ε 3.9 and 3.39); δ (100 MHz) 1.17 (d, *J* 8 Hz, 3 H, CH_3), 1.30—2.66 (m, 10 H), 2.82—3.02 (m, 2 H, $ArCH_2$), 3.66 (s, 3 H, CO_2CH_3), 3.82 (s, 3 H, $ArOCH_3$), 7.06—7.18 (m, 2 H, ArH), and 7.58 (d, *J* 2 Hz, 1 H, ArH, *o*-COArH); *m/z* (relative intensity) 304 (M^+, 8), 272 (4), 245 (3), 189 (8), 176 (100), 161 (11), 149 (14), 119 (96), 120 (20), 91 (14), 77 (13), 69 (14), 59 (24), and 41 (42).

Hydrogenolysis of the Keto Ester (**19a**) *to give Methyl* 11-*Methyl-5,6,7,8,9,10,11,12-octahydrobenzocyclodecene-7-carboxylate* (**20a**).—A solution of compound (**19a**) (90 mg, 0.33 mmol) in methanol (10 ml) containing aqueous $HClO_4$ (0.25 ml, 70%) was hydrogenated at room temperature and atmospheric pressure in the presence of Pd–C (100 mg, 10%) for 16 h. The catalyst was filtered off and washed with methanol. The filtrate and the washings were neutralised with 5% aqueous Na_2CO_3, and the alcohol was distilled off. The organic material was extracted with ether, washed with water, and dried (Na_2SO_4). After removal of the solvent, the residue on evaporative distillation at 160 °C (bath-temp.) (0.2 mmHg) afforded the ester (**20a**) (80 mg, 94%); homogeneous in g.l.c. (Found: C, 78.4; H, 9.2. $C_{17}H_{24}O_2$ requires C, 78.42; H, 9.29%); ν_{max} 2 910, 2 860, 1 735, 1 495, 1 450, 1 435, 1 375, 1 200, and 1 110 cm^{-1}; δ(CCl_4) 1.1 (d, *J* 8 Hz, 3 H, CH_3), 1.27—2.6 (m, 10 H), 2.61—3.0 (m, 4 H, $ArCH_2$), 3.57 (s, 3 H, CO_2CH_3), and 6.87 (s, 4 H, ArH).

Formylation of the Hydroxycyclopentanone (**4b**) *to give Ethyl 4-Methyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthren-10a-yl(hydroxymethylene)acetate* (**21**).—Formylation of compound (**4b**) (500 mg, 1.75 mmol) in benzene (10 ml) with NaH (700 mg, 29 mmol) and ethyl formate (2.5 ml, 30.5 mmol) following the procedure described for compound (**6a**) afforded a pale yellow solid, which on chromatography over alumina (10 g) using petroleum as eluant afforded the *ester* (**21**) (450 mg, 75%), m.p. 117 °C (petroleum) as a colourless solid (Found: C, 73.6; H, 7.65. $C_{21}H_{26}O_4$ requires C, 73.66; H, 7.66%); ν_{max} 3 000, 2 960, 2 920, 2 860, 2 830, 1 655, 1 610, 1 595, 1 570, 1 500, 1 460, 1 430, 1 300, 1 275, 1 165, 1 060, 960, 910, 840, and 820 cm^{-1}; λ_{max} 256 nm (log ε 4.2); δ (CCl_4), 1.33 (t, *J* 7 Hz, 3 H, $CO_2CH_2CH_3$), 1.9 (br s, 3 H, $C{=}CCH_3$), 1.97—2.8 (m, 10 H), 3.7 (s, 3 H, $ArOCH_3$), 4.23 (q, *J* 7 Hz, 2 H, $CO_2CH_2CH_3$), 6.76 (d, *J* 12 Hz, 1 H, =CHOH), 6.47—7.13 (m, 3 H, ArH), and 11.8 (d, *J* 12 Hz, =CHOH, exchangeable with D_2O); *m/z* (relative intensity) 342 (M^+, 59), 296 (46), 281 (17), 268 (45), 251 (31), 239 (27), 228 (82), 226 (75), 211 (100), and 164 (65).

Hydrolysis and Esterification of Compound (**21**) *to give Methyl 4-Methyl-7-methoxy-1,2,3,9,10,10a-hexahydrophenanthren-10a-ylacetate* (**22**).—A solution of compound (**21**) 250 mg, 0.73 mmol) in ethanol (25 ml) was refluxed under N_2 for 4 h with a solution of KOH (2.5 g, 45 mmol) in water (2.5 ml). After the usual work-up, the aqueous alkaline layer was acidified with 6M-HCl and the acidic material was extracted with ether. The crude acid was esterified with CH_2N_2 in ether and the resulting ester was chromatographed on alumina (4 g) using petroleum as eluant to afford the methyl ester (**22**) (165 mg, 75%) as a colourless liquid; ν_{max} 3 000, 2 840, 1 725, 1 600, 1 490, 1 450, 1 430, 1 270, 1 160, and 1 040 cm^{-1}; δ(CCl_4) 1.82 (s, 3 H, CH_3), 1.23—2.2 (m, 12 H), 3.53 (s, 3 H, CO_2CH_3), 3.73 (s, 3 H, $ArOCH_3$), and 6.46—7.1 (m, 3 H, ArH).

Crystal Structure Analysis of Hydroxy γ-Lactonic Acid (**12a**).—*Crystal data.* $C_{18}H_{20}O_5$, *M* = 316; Orthorhombic, space group $P2_12_12_1$; *a* = 10.210 (1), *b* = 15.674 (2), *c* = 9.407 (1) Å; *Z* = 4; D_m = 1.393, D_c = 1.394 g cm^{-3}; *F*(000) = 672; μ(Cu-K_α) = 8.5 cm^{-1}. 1 622 Independent reflections were measured by ω − 2θ scan on a CAD-4 diffractometer, in the range $2 < \theta \leqslant 60°$ using graphite-monochromated Cu-K_α radiation.

The structure was solved by MULTAN 78.[17] While full-matrix least-squares refinement was carried out at the initial stage, block-diagonal approximation was used after introducing the anisotropic thermal parameters for C and O atoms. In the final cycles a weighting scheme reflecting the trends in $|\Delta F|$ was used.[18] and the refinement converged at $R = 0.049$, $R_w = 0.051$ and $S = 1.03$ for all 1 622 reflections. A final difference map showed peaks with maximum and minimum heights of 0.2 and −0.2 e $Å^{-3}$ respectively.

A view of the molecule projected down the *c* axis is shown in Figure 1. The positional parameters of the C and O atoms are given in Table 1, and selected bond distances and angles in Table 2.

Crystal Structure Analysis of the Hydroxymethylene Ester (**21**).—*Crystal data.* $C_{21}H_{26}O_4$, *M* = 342, Orthorhombic space group $Pn2_1a$, *a* = 22.818 (11), *b* = 12.333 (4), *c* = 6.577 (2) Å, *Z* = 4, D_m = 1.24 g cm^{-3}, D_c = 1.23 g cm^{-3}, *F*(000) = 736, μ(Mo-K_α) = 0.905 cm^{-1}. The intensities of 1 131 observed reflections with $|F| \geqslant 4\,\sigma(|F|)$ and $\theta \leqslant 25°$ were measured by ω − 2θ scan on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation.

The structure was solved by MULTAN-78 [17] and was refined initially with isotropic temperature factors, and anisotropically

Table 1. Positional parameters (× 10^4) of the non-hydrogen atoms in the asymmetric unit of the hydroxy γ-lactonic acid (**12a**) (Figure 1) with e.s.d.s in parentheses

	x	*y*	*z*
C(1)	7 193(3)	2 056(2)	2 175(4)
C(2)	7 169(3)	2 946(2)	2 815(4)
C(3)	5 962(3)	3 432(2)	2 320(3)
C(4)	4 681(3)	2 986(2)	2 762(3)
C(4a)	4 677(3)	2 040(2)	2 212(3)
C(4b)	3 469(3)	1 532(2)	2 627(3)
C(5)	2 314(3)	1 625(2)	1 861(4)
C(6)	1 203(3)	1 149(2)	2 157(4)
C(7)	1 267(4)	552(2)	3 263(5)
C(8)	2 404(4)	454(2)	4 033(4)
C(8a)	3 530(3)	938(2)	3 735(3)
C(9)	4 758(4)	774(2)	4 565(4)
C(10)	6 034(3)	1 128(2)	3 963(4)
C(10a)	5 953(3)	1 529(2)	2 477(3)
C(11)	5 783(3)	859(2)	1 285(4)
C(12)	5 255(3)	1 411(2)	84(3)
C(13)	4 508(3)	3 003(2)	4 389(3)
C(14)	3 540(3)	3 459(2)	2 075(3)
O(15)	5 343(2)	1 306(2)	−1 179(2)
O(16)	4 655(2)	2 100(1)	627(2)
O(17)	6 865(3)	368(1)	912(3)
O(18)	2 460(2)	3 454(1)	2 835(2)
O(19)	3 619(2)	3 813(1)	931(2)

Table 2. Bond distances (Å) and angles (°) in the asymmetric unit of the hydroxy γ-lactonic acid (**12a**) (Figure 1) with e.s.d.s in parentheses

(a) Bond distances (Å)

C(1)–C(2)	1.520(4)	C(6)–C(7)	1.400(5)
C(1)–C(10a)	1.538(4)	C(7)–C(8)	1.377(5)
C(2)–C(3)	1.522(4)	C(8)–C(8a)	1.406(5)
C(3)–C(4)	1.540(4)	C(8a)–C(9)	1.499(5)
C(4)–C(13)	1.541(4)	C(9)–C(10)	1.525(5)
C(4)–C(4a)	1.571(3)	C(10)–C(10a)	1.535(4)
C(4)–C(14)	1.525(4)	C(10a)–C(11)	1.545(4)
C(4a)–C(10a)	1.549(4)	C(11)–C(12)	1.522(4)
C(4a)–O(16)	1.494(3)	C(11)–O(17)	1.392(4)
C(4a)–C(4b)	1.519(4)	C(12)–O(15)	1.203(4)
C(4b)–C(8a)	1.399(4)	C(14)–O(18)	1.314(4)
C(4b)–C(5)	1.389(4)	C(14)–O(19)	1.214(4)
C(5)–C(6)	1.387(5)	C(12)–O(16)	1.392(3)

(b) Bond angles (°)

C(3)–C(4)–C(4a)	110.2(2)	C(8)–C(7)–C(6)	120.4(4)
C(3)–C(4)–C(13)	111.0(2)	C(7)–C(6)–C(5)	118.1(3)
C(3)–C(4)–C(14)	108.3(2)	C(6)–C(5)–C(4b)	122.2(3)
C(4a)–C(4)–C(13)	110.1(2)	C(8a)–C(4b)–C(5)	119.7(3)
C(4a)–C(4)–C(14)	108.5(2)	C(8a)–C(4b)–C(4a)	120.2(2)
C(13)–C(4)–C(14)	109.0(2)	C(5)–C(4b)–C(4a)	120.0(2)
C(4)–C(3)–C(2)	112.3(2)	C(4)–C(4a)–C(10a)	115.6(2)
C(3)–C(2)–C(1)	110.6(3)	C(4)–C(4a)–C(4b)	114.3(2)
C(2)–C(1)–C(10a)	114.3(2)	C(4)–C(4a)–O(16)	105.6(2)
C(1)–C(10a)–C(10)	110.1(2)	C(10a)–C(4a)–C(4b)	111.8(2)
C(1)–C(10a)–C(4a)	112.7(2)	C(4b)–C(4a)–O(16)	106.1(2)
C(1)–C(10a)–C(11)	108.8(2)	C(11)–C(12)–O(16)	110.0(2)
C(10)–C(10a)–C(4a)	113.8(2)	C(11)–C(12)–O(15)	129.0(3)
C(10)–C(10a)–C(11)	112.8(2)	O(16)–C(12)–O(15)	121.4(3)
C(4a)–C(10a)–C(11)	98.0(2)	C(10a)–C(11)–C(12)	101.1(2)
C(10a)–C(10)–C(9)	116.2(3)	C(10a)–C(11)–O(17)	118.0(3)
C(10)–C(9)–C(8a)	117.3(3)	C(12)–C(11)–O(17)	114.1(3)
C(9)–C(8a)–C(8)	119.2(3)	C(4)–C(14)–O(19)	123.2(2)
C(9)–C(8a)–C(4b)	122.7(3)	C(4)–C(14)–O(18)	114.1(2)
C(8)–C(8a)–C(4b)	118.1(3)	O(19)–C(14)–O(18)	122.8(3)
C(8a)–C(8)–C(7)	121.6(3)	C(4a)–O(16)–C(12)	108.8(2)

Table 3. Positional parameters ($\times 10^4$) of the non-hydrogen atoms in the asymmetric unit of the hydroxymethylene ester (**21**) (Figure 2) with e.s.d.s in parentheses

	x	*y*	*z*
C(1)	4 310(3)	1 341(7)	−351(15)
C(2)	4 486(4)	1 072(7)	−2 481(15)
C(3)	4 943(4)	1 881(7)	−3 178(13)
C(4)	4 813(3)	3 037(6)	−2 572(12)
C(4a)	4 356(3)	3 316(6)	−1 372(11)
C(4b)	4 161(3)	4 472(6)	−991(11)
C(5)	4 221(3)	5 281(6)	−2 469(12)
C(6)	4 035(3)	6 318(7)	−2 156(12)
C(7)	3 758(3)	6 591(7)	−342(12)
C(8)	3 671(3)	5 781(7)	1 109(12)
C(8a)	3 861(3)	4 739(6)	788(12)
C(9)	3 711(3)	3 886(7)	2 375(12)
C(10)	4 031(3)	2 827(7)	2 059(12)
C(10a)	4 006(3)	2 460(6)	−193(11)
C(11)	3 377(3)	2 391(6)	−1 024(11)
C(12)	3 243(3)	2 857(6)	−2 810(11)
C(13)	2 915(3)	1 791(7)	17(13)
C(14)	2 611(4)	591(8)	2 640(15)
C(15)	2 900(5)	−20(10)	4 368(19)
C(16)	3 557(6)	8 431(8)	−1 396(17)
C(17)	5 269(3)	3 830(8)	−3 389(14)
O(18)	3 547(2)	7 598(5)	134(9)
O(19)	2 393(2)	1 802(6)	−561(10)
O(20)	3 076(2)	1 203(5)	1 639(8)
O(21)	2 717(2)	2 856(5)	−3 715(8)

Table 4. Bond distances (Å) and angles (°) in the asymmetric unit of the hydroxymethylene ester (**21**) (Figure 2) with e.s.d.s in parentheses

Bond distances (Å)

C(1)–C(10a)	1.495(14)	C(10)–C(10a)	1.550(11)
C(1)–C(2)	1.548(11)	C(10a)–C(4a)	1.534(10)
C(2)–C(3)	1.515(12)	C(10a)–C(11)	1.538(10)
C(3)–C(4)	1.510(12)	C(4a)–C(4b)	1.513(11)
C(4)–C(4a)	1.353(10)	C(4b)–C(8a)	1.395(10)
C(4)–C(17)	1.527(12)	C(11)–C(13)	1.458(11)
C(5)–C(6)	1.364(11)	C(11)–C(12)	1.343(10)
C(5)–C(4b)	1.400(11)	C(12)–O(21)	1.339(9)
C(6)–C(7)	1.391(11)	C(13)–O(19)	1.250(9)
C(7)–C(8)	1.396(12)	C(13)–O(20)	1.341(10)
C(7)–O(18)	1.368(10)	C(14)–C(15)	1.514(15)
C(8)–C(8a)	1.372(11)	C(14)–O(20)	1.458(10)
C(9)–C(10)	1.510(12)	C(16)–O(18)	1.438(12)
C(9)–C(8a)	1.521(11)		

(b) Bond angles (°)

C(2)–C(1)–C(10a)	112.4(7)	C(9)–C(8a)–C(4b)	121.5(7)
C(1)–C(2)–C(3)	108.8(7)	C(10)–C(9)–C(8a)	113.3(7)
C(2)–C(3)–C(4)	114.0(7)	C(9)–C(10)–C(10a)	111.5(6)
C(3)–C(4)–C(4a)	123.1(7)	C(1)–C(10a)–C(10)	107.9(6)
C(3)–C(4)–C(17)	112.2(7)	C(1)–C(10a)–C(4a)	110.3(6)
C(4a)–C(4)–C(17)	124.6(7)	C(1)–C(10a)–C(11)	110.2(6)
C(4)–C(4a)–C(10a)	121.3(6)	C(10)–C(10a)–C(4a)	105.2(6)
C(4)–C(4a)–C(4b)	124.2(6)	C(10)–C(10a)–C(11)	112.9(6)
C(10a)–C(4a)–C(4b)	114.4(6)	C(4a)–C(10a)–C(11)	110.1(6)
C(5)–C(4b)–C(4a)	121.8(6)	C(10a)–C(11)–C(13)	122.3(6)
C(5)–C(4b)–C(8a)	117.5(7)	C(10a)–C(11)–C(12)	120.0(6)
C(4a)–C(4b)–C(8a)	120.4(6)	C(13)–C(11)–C(12)	117.6(7)
C(6)–C(5)–C(4b)	122.3(7)	C(11)–C(12)–O(21)	126.3(7)
C(5)–C(6)–C(7)	119.8(7)	C(11)–C(13)–O(19)	122.7(7)
C(6)–C(7)–C(8)	118.5(7)	C(11)–C(13)–O(20)	116.8(7)
C(6)–C(7)–O(18)	125.1(7)	O(19)–C(13)–O(20)	120.5(7)
C(8)–C(7)–O(18)	116.3(7)	C(15)–C(14)–O(20)	106.3(7)
C(7)–C(8)–C(8a)	121.3(7)	C(7)–O(18)–C(16)	118.8(7)
C(8)–C(8a)–C(9)	118.1(7)	C(13)–O(20)–C(14)	116.2(6)
C(8)–C(8a)–C(4b)	120.4(7)		

at a later stage to a final $R = 0.056$, $R_w = 0.041$, $S = 1.76$. The view of the asymmetric unit is shown in Figure 2. The rings consisting of C(1)–C(2)–C(3)–C(4)–C(4a)–C(10a) and C(9)–C(10)–C(10a)–C(4a)–C(4b)–C(8a) are of half-sofa and half-chair conformations, respectively.

The positional parameters are given in Table 3 and bond distances and angles in Table 4.

Tables of (i) the anisotropic thermal parameters of C and O atoms, and (ii) the refined co-ordinates and fixed isotropic temperature factors of H atoms for both compounds (**12a**) and (**21**) are given in a Supplementary Publication [SUP No. 56130 (5 pp.)].* The observed and calculated structure factors for each compound are available on request from the editorial office.

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* For details of the Supplementary Publications Scheme see Instructions for Authors (1985) in *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

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