Correlation of Ring-junction Stereochemistry in A-Aromatic Octahydrophenanthrenes with ^{13}C N.M.R. Chemical Shifts

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More than twenty synthetic derivatives of structurally established A-aromatic octahydrophenanthrenes were examined by ^{13}C n.m.r. Empirical observations were made on the experimental chemical-shift trends at C-1, C-6, C-9, and C-10, which are sufficiently characteristic to allow probable assignment of the stereochemistry of the B/C ring junction.

The A-aromatic octahydrophenanthrene ring system is widely found in certain alkaloids and steroids. In contrast to its skeletal simplicity, determination of the steric arrangement of the B/C rings often requires extensive chemical and spectral manipulation. However, in 1964 we reported [1] that ^1H n.m.r. spectroscopy provides a convenient and useful method for assigning the B/C ring fusion stereochemistry of octahydrophenanthrenes such as (I) including three typical conformations, (A), (B), and (C). This arose from our earlier finding that the degree of the steric compression between the C-1 and C-11 *peri*-hydrogens depending on the ring conformations is closely related to the magnitude of the deshielding effect on the C-1 aromatic hydrogen. The effect has conveniently been expressed by the chemical-shift difference between the C-1 and C-4 hydrogens, $\Delta\delta$ $H_1 - H_4$. Thus, somewhat larger $\Delta\delta$ $H_1 - H_4$ values of 0.5—0.6 p.p.m. were observed for the B/C-*trans*-compounds (IA) and the B/C-*cis*-compounds of type (IB), while the corresponding values of 0.4—0.5 p.p.m. were obtained for the B/C-*cis*-compounds of type (IC). Both parameters, despite being slightly different, hold true for compounds of this series which have hitherto been examined.[2] Nevertheless, this approach could not be used to clearly distinguish between conformers (IA) and (IB) without recourse to additional evidence.

^{13}C N.m.r. was expected to be more useful than ^1H n.m.r. in view of the magnitude of the carbon shift and its susceptibility to structural changes. The present paper reports the potential utility of ^{13}C n.m.r. spectroscopy for assignment of the B/C ring-junction stereochemistry of A-aromatic octahydrophenanthrenes.

Results and Discussion

The present study examined twenty-four A-aromatic octahydrophenanthrene derivatives (1)—(24), all of which are racemic with the exception of natural estrone and estradiol 3-methyl ethers (1) and (2). Of these, the tetracyclic compounds were available from our previous studies [3,4] and the tricyclic ones were prepared by conventional methods. Their stereostructures were established on the basis of the stereochemical principle of synthetic reactions, chemical relationships with structurally known compounds, a variety of spectral data, and/or *X*-ray crystallographic analyses.[5]†

Although the B/C-*trans*-compounds (1)—(8) are believed to adopt the rigid conformation of (IA), the B/C-*cis*-compounds (9)—(24) may exist as an equilibrium mixture of conformers (IB) and (IC). In particular, the conformation of the tricyclic systems which is more flexible than that of the tetracyclic ones tends to achieve a favourable geometry to minimize the steric interactions.

Compounds (15) and (16) are believed to exclusively exist as the most stable conformer (IC) which avoids the sole steric compression between the *peri*-hydrogens. This is consistent with the ^1H n.m.r. observation on the $\Delta\delta$ $H_1 - H_4$ values (see below).

The alcohols (9) and (17), (10) and (18), or (11) and (19) were obtained together as the C-13 epimeric pairs by hydride reduction or different Grignard reactions of the ketone (16). The ^1H n.m.r. data clearly show that the epimeric pairs are likely to exist in different ring conformations. Alcohols (9), (10), and (11) show the $\Delta\delta$ $H_1 - H_4$ values of 0.5—0.6 p.p.m. associated with conformation (IB). On the other hand, epimers (17), (18), and (19) exhibit the corresponding values of 0.4—0.5 p.p.m. accepted for conformation (IC). Further evidence came from the free OH stretching infrared absorption data,[6,7] indicating that the alcohol epimers (9) and (17) both have an equatorial hydroxy group (see Experimental section). This fact also suggests that the epimers differ in their skeletal conformations, probably because of a delicate steric balance between the C-13 hydroxy group and the opposing *peri*-hydrogens. In the case of compounds (10) and (18), or (11) and (19), the more bulky C-13 alkyl groups are expected to preferentially adopt an equatorial position in either conformation. Thus, the ring conformations including the C-13 stereochemistry of the B/C-*cis*-tricyclic compounds could be reasonably assigned.

Also in the tetracyclic series, careful spectral inspection and conformational consideration including the D-ring system led to the conclusion that compounds (12), (13), and (14) must exist as form (IB), whereas compounds (20), (21), (22), (23), and (24) must adopt form (IC).

All of the above-mentioned compounds were examined by ^{13}C n.m.r. spectra. The signal assignments were normally based upon signal multiplicities obtained from single-frequency off-resonance decoupling (SFORD) spectra and

† For the oxa-steroid, *X*-ray crystallographic analysis has very recently been carried out on the 8,9-dehydro derivative of compound (12): monoclinic crystals, space group $P2_1/C_1$, a = 11.764(1), b = 15.796(1), c = 14.790(2) Å, β = 146.00(1°), Z = 4. On refinement (all H atoms included) the conventional R value converged to R = 0.058 for 1 550 reflections.

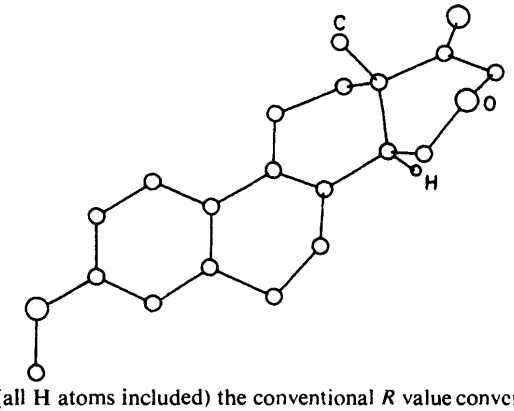
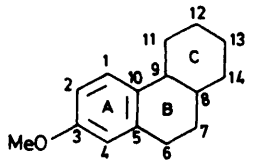


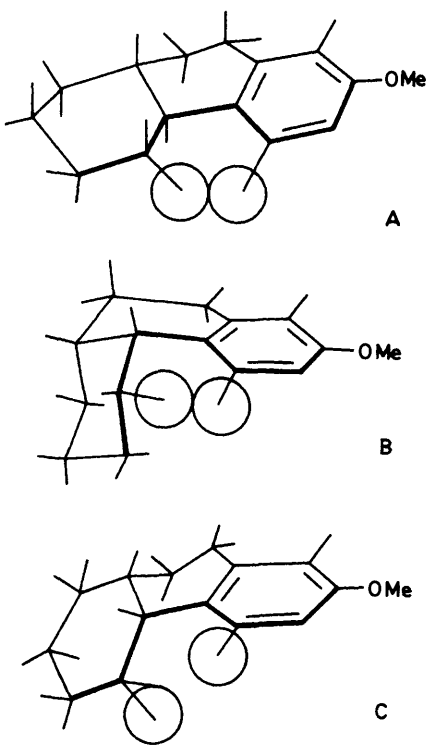
Table 1. ^{13}C Chemical shift assignments for compounds (1)—(27) *

Type	Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	OMe	COMe	$\Delta C_1 - C_4$ ($\Delta H_1 - H_4$)
(IA)	(1)	126.3	111.6	157.6	113.9	137.7	29.7	26.5	38.4	44.0	132.0	25.9	31.6	48.0	50.4	21.6	35.8	220.7	13.8	55.2		12.4 (0.56)
	(2)	126.3	111.5	157.5	113.8	137.9	29.8	26.3	38.9	44.0	132.7	27.3	36.7	43.3	50.1	23.1	30.6	81.9	11.0	55.2		12.5 (0.58)
	(3)	126.4	111.6	157.4	113.8	138.4	30.3	30.3 [a]	41.0	43.4	133.0	30.8 [a]	26.4 [b]	27.0 [b]	31.3					55.2		12.6 (0.58)
	(4)	126.6	111.7	157.6	113.8	138.2	30.3 [a]	30.2 [a]	38.9	43.1	131.9	29.2	36.0	70.5	42.3					55.2		12.8 (0.56)
	(5)	126.1	111.7	157.6	113.5	137.4	29.7	25.7 [a]	36.6	43.1	132.4	26.4 [a]	35.1	37.6	48.0	65.0	66.9	75.6	10.1	55.2		12.6 (0.57)
	(6)	126.3	111.7	157.6	113.4	137.6	30.0	24.3	38.9	43.0	132.5	26.5	36.4	38.9	51.7	26.0	28.4	79.0	10.3	55.2		12.9 (0.57)
	(7)	126.3	111.7	157.5	113.4	137.5	29.9	24.9	39.0	43.3	132.5	26.0	35.4	37.4	43.3	26.0	30.7	72.1	16.5	55.2		12.9 (0.58)
	(8)	127.1	111.9	157.5	113.7	137.8	28.4 [a]	23.5 [b]	36.6	38.6	132.7	27.2	31.1 [a]	39.2	49.7	23.2 [b]	29.2 [a]	78.1	22.8	55.2		13.4 (0.57)
(IB)	(9)	127.9	112.2	157.4	113.7	137.9	26.7 [a]	27.5 [a]	33.9	36.7	130.9	27.4 [a]	31.1	69.8	36.3					55.1		14.2 (0.54)
	(10)	127.7	112.0	157.4	113.8	138.3	26.6	27.6	31.0	36.2	129.9	24.9	34.4	70.0	39.5	31.3				55.1		13.9 (0.59)
	(11)	127.2	111.9	157.2	113.8	138.3	25.9	28.2	30.2	35.5	129.4	24.1	25.5	75.7	30.6	37.7	25.0			55.1		13.4 (0.60)
	(12)	127.3	112.3	157.6	114.0	138.0	25.5	23.2	33.2	37.1	129.0	24.8	26.9	45.2	35.3	65.7	70.2	213.9	15.4	55.2		13.3 (0.59)
	(13)	127.2	112.2	157.3	113.9	138.4	25.4	23.5	31.6	37.4	129.6	25.4	30.1	37.8	39.5	65.1	67.1	75.3	10.0	55.2		13.3 (0.58)
	(14)	127.2	112.3	157.5	114.0	138.2	25.3	23.3	31.6	37.4	129.4	25.3	30.0	36.9	39.7	65.1	64.1	76.3	11.0	55.2	170.4 20.9	13.2 (0.57)
(IC)	(15)	129.5	111.9	157.3	113.4	137.3	29.9	23.9	34.1	39.5	134.6	31.4	26.1	21.6	32.0					55.1		16.1 (0.41)
	(16)	129.4	112.4	157.9	113.6	136.7	28.9	24.8	37.1	38.0	131.3	32.2	40.3	211.6	46.2					55.2		15.8 (0.46)
	(17)	130.0	112.1	157.5	113.4	137.1	30.3	24.3	34.5	38.7	133.4	30.8	35.8	66.8	40.9					55.2		16.6 (0.41)
	(18)	129.3	112.1	157.4	113.5	137.7	29.8	27.6	33.9	38.5	132.7	26.3	38.2	70.0	42.8	30.7				55.1		15.8 (0.47)
	(19)	130.0	112.1	157.4	113.3	137.6	31.5 [a]	28.1	34.2	39.7	134.2	26.2	31.6 [a]	75.3	36.0	38.0	25.2			55.1		16.7 (0.42)
	(20)	130.0	112.4	157.7	113.3	137.0	31.3	21.8	36.7	40.7	133.2	27.8	32.5	45.6	44.2	65.9	70.8	212.6	18.4	55.2		16.7 (0.41)
	(21)	129.9	112.3	157.5	113.2	137.3	31.3	22.0	36.7	40.9	133.6	28.0	37.2	37.2	46.1	67.2	67.8	76.3	11.8	55.2		16.7 (0.42)
	(22)	130.0	112.3	157.5	113.2	137.2	31.3	21.9	36.6	40.7	133.5	27.8	37.1	36.6	46.2	67.1	64.7	77.0	13.0	55.2	170.4 20.9	16.8 (0.42)
	(23)	129.4	112.2	157.4	113.4	137.8	30.2 [a]	27.8 [a]	40.5	36.5	132.6	27.6 [a]	27.6 [a]	37.6	46.6	30.7 [a]	29.4 [a]	77.0	25.8	55.2		16.0 (0.48)
	(24)	129.8	112.3	157.5	113.4	137.6	30.0 [a]	27.9 [a]	42.2	36.2	132.8	28.1 [a]	28.1 [a]	37.1	48.9	31.3 [a]	26.4 [a]	79.2	25.0	55.2	170.5 21.2	16.4 (0.45)
	(25)	129.9	111.8	157.5	113.7	138.1	29.8	23.5 [a]	23.2 [a]	28.6	134.5									55.1		16.2 (0.39)
	(26)	128.9	112.0	157.4	113.5	138.0	30.4	20.6	31.8	31.8	134.4	22.9								55.1		15.4 (0.49)
	(27)	129.5	111.8	157.3	113.5	138.3	30.2	20.0	27.3	38.5	133.6	29.5	11.8							55.1		16.0 (0.48)

* The same carbon numbering as in the steroidal series has been adopted to facilitate the comparison of chemical shifts (δ/p.p.m.). [a,b] Assignments may be interchanged in each horizontal row.



(I)



known chemical-shift rules [8,9] (*e.g.*, acetylation shift [10] and steric γ- and δ-effects [11]). Further assistance was obtained by comparison with data of compounds (1) and (2) [12-14] and reference compounds (25), (26), and (27). For the three methine carbons, the doublet signal due to the C-9 carbon was differentially assignable from SFORD spectra irradiated at the ^1H signal of tetramethylsilane (TMS) on the basis that the residual J value of the C-9 signal is larger than that of the C-8 or C-14 signal, since the C-9 proton resonance (δ 2.5—3.0) appears at lower fields compared to the C-8 or C-14 proton resonance (δ 1.5—2.3). The assignment for several of the methine and methylene carbons, although relatively complicated, was supported also by comparison of the observed chemical shifts with the calculated ones derived using various substituent parameters.[15] The assignments made on these bases are given in Table 1.

The discussion will now be confined to the C-1 through C-14 carbon atoms associated with the octahydrophenanthrene ring skeleton although we excluded any C-13 and C-14 carbons under the influence of the additional ring moiety or substituents (α-substituent effect).

The chemical shifts observed for the C-7, C-8, C-11, and C-12 carbons also could not be evaluated substantially without the effects of substituents attached to the C-13 and C-14 carbons (β- and γ-substituent effects). On the other hand, the aromatic C-2, C-3, C-4, and C-5 carbon resonances display no significant differences among the compounds studied here.

Table 2. ^{13}C Chemical shift ranges of C-1, C-6, C-9, and C-10 in different B/C ring junctions

B/C Ring junction	C-1	C-6	C-9	C-10	Δ $C_1 - C_4$
trans (IA)	126—127	28—31	43—44	132—133	12—14
cis (IB)	127—128	25—27	35—38	129—131	13—14
cis (IC)	129—130	29—32	38—41	131—135	15—17

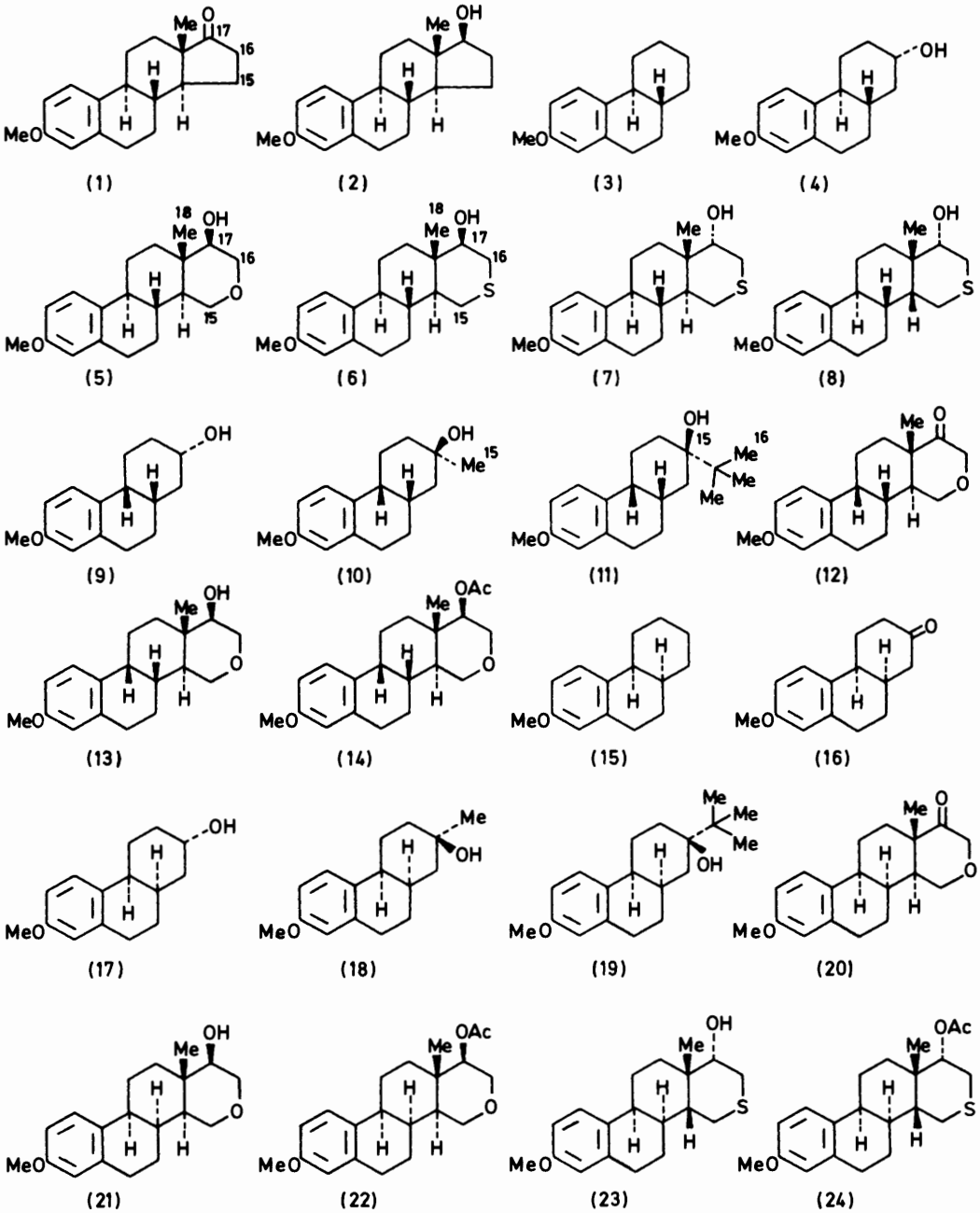
The signal values for the remaining C-1, C-6, C-9, and C-10 carbons, which are moderately sensitive to structural modification, seem to be parameters of choice which correlate them directly with the B/C ring-junction configurations. These data are summarized in Table 2, which can be used diagnostically to predict the ring stereochemistry of the octahydrophenanthrene system.

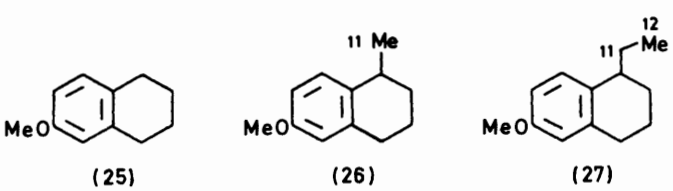
The differentiation of the B/C-*trans*-compounds (IA) from the B/C-*cis*-compounds of type (IC) can be readily made on the basis of the C-1 chemical shift. Also, the C-1 resonance allows a distinction between both conformations (IB) and (IC) for the B/C-*cis*-compounds. In such cases, the $\Delta\delta$ $C_1 - C_4$ value may be used to substitute for the $\Delta\delta$ $H_1 - H_4$ value. However, a clear distinction between the B/C-*trans*-form (IA) and the B/C-*cis*-form (IB) cannot be based on only the C-1 signal. This conformational assignment can be made by examining the chemical shift ranges for the C-6 and C-10 carbons. These signals both appear downfield in forms (IA) and (IC) relative to form (IB) by *ca.* 2—5 p.p.m. The data for the C-9 carbon may also be utilized, but they should be carefully inspected. For instance, the signal values for compounds (8), (23), and (24) should be eliminated from the standard, because the C-9 carbons in these compounds experience shielding effects due to the γ-*gauche* interactions with the C-15 carbons, thus resulting in the observed deviation of the chemical-shift values.

In conclusion, this study shows that the empirically observed chemical-shift values for some carbon atoms of A-aromatic octahydrophenanthrene systems are quite useful for predicting and assigning the B/C ring-fusion configurations. Furthermore, significant conformational changes such as those found in the B/C-*cis*-octahydrophenanthrenes in going from the parent ketone (16) to the alcohol derivatives (9), (10), and (11), caused by steric interactions, can be discerned by ^{13}C n.m.r. spectroscopy. We also confirmed that the signals ascribed to the C-6 and C-8 carbons in compounds (1) and (2) were correctly assigned by Reich *et al.*[12] but mistakenly by Wittstruck and Williams,[13] as Blunt and Stothers [9] have reported.

Experimental

M.p.s were determined on a calibrated Köfler hot-stage apparatus. I.r. spectra were recorded on a JASCO-A-702 spectrophotometer and u.v. spectra on Hitachi EPS-3T spectrophotometer. ^1H N.m.r. spectra were taken on a Varian A-60 instrument using TMS as internal standard. ^{13}C N.m.r. spectra were taken at 15.087 MHz with a Varian NV-14 Fourier Transform (F.T.) n.m.r. spectrometer. F.T. measurement conditions were as follows: spectral width, 3 923 Hz; number of data points, 4 820; pulse width, 12 μs (pulse flipping angle, 18°); acquisition time, 0.6 s; number of transients, 15 000—130 000. The samples were normally examined as 0.1—0.3M-solutions in deuteriochloroform using TMS as internal standard in 8-mm spinning tubes. The accuracies of the ^{13}C and ^1H chemical shifts and the ^1H coupling constants are within ±0.1 and ±0.01 p.p.m. and ±0.5





Hz, respectively. Preparative t.l.c. was carried out on 100 × 20 × 0.075-cm glass plates coated with silica gel GF_{254} (type 60; Merck). Usual work-up means washing extracts with water and then brine, drying (Na_2SO_4), filtration, and evaporation under reduced pressure. Ether refers to diethyl ether throughout.

Catalytic Hydrogenation of 7-Methoxy-3,4,9,10-tetrahydrophenanthren-2(1H)-one.—A solution of 7-methoxy-3,4,9,10-tetrahydro-2(1*H*)-phenanthrenone [16] (10 g, 43.8 mmol) in dry ethanol (550 ml) was hydrogenated over 5% palladium–charcoal (4 g) at room temperature and atmospheric pressure. After 2 h the hydrogenation was complete and the catalyst was filtered off. The solvent was removed under reduced pressure and the oily residue was crystallized from ether–pentane to give *7-methoxy-3,4,4aα,9,10,10aα-hexahydrophenanthren-2(1H)-one* (16) (7.85 g, 77.8%), m.p. 90—91 °C. Recrystallization from 95% ethanol afforded an analytical sample, m.p. 91—93 °C, $\nu_{max.}$ (CCl_4) 1 715 cm^{-1}; δ($CDCl_3$) 3.77 (3 H, s, OMe), 6.64 (1 H, bs, 8-H), 6.76 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.10 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 78.45; H, 8.0. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%).

Lithium Aluminium Hydride Reduction of 7-Methoxy-3,4,9,-10-tetrahydrophenanthren-2(1H)-one.—To a stirred solution of lithium aluminium hydride (1.5 g) in dry tetrahydrofuran

(15 ml) was slowly added a solution of 7-methoxy-3,4,9,10-tetrahydrophenanthren-2(1*H*)-one [16] (1 g, 4.38 mmol) in dry tetrahydrofuran (15 ml). After the mixture had been left at room temperature overnight, the excess of hydride was decomposed by adding acetone followed by water. The mixture was then extracted with dichloromethane. After usual work-up, the oily residue was crystallized from ether–pentane to yield 7-*methoxy*-1,2,3,4,9,10-*hexahydrophenanthren*-2-*ol* (739.2 mg, 73.3%), m.p. 90—93 °C. The analytical sample was obtained by recrystallization from acetone–ether, m.p. 95—96 °C, $\lambda_{max.}$ (EtOH) 271.5 nm (ε 16 200) (Found: C, 78.45; H, 8.05. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.88%).

7-*Methoxy*-1,2,3,4,4aα,9,10,10aα-*octahydrophenanthren*-2-*ols* (9) *and* (17).—(*a*) A solution of the phenanthrenone (16) (440 mg, 1.91 mmol) in methanol (20 ml) was treated with sodium borohydride (360 mg) in water (5 ml) under stirring. After being left overnight, the mixture was carefully poured into cold dilute hydrochloric acid solution and extracted with ether. The extract was washed with aqueous sodium carbonate and then worked up as usual. The resultant oily residue was purified by preparative t.l.c. [benzene–ethyl acetate (4 : 1) with double development], affording the 2β-*alcohol* (9) (235.6 mg, 53.1%) and the 2α-*alcohol* (17) (48.8 mg, 11.0%). Both analytical samples were obtained by recrystallization from ether–pentane. The 2β-alcohol (9) had m.p. 78—80 °C, $\nu_{max.}$ (CCl_4) [6,7] 3 622.9 cm^{-1} with $\Delta\nu_{1/2}$ 22.4 cm^{-1} and α : β 0.87; δ($CDCl_3$) 3.76 (3 H, s, OMe), 6.63 (1 H, bs, 8-H), 6.73 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.17 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 77.3; H, 8.9. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%). The 2α-alcohol (17) had m.p. 89—90 °C, $\nu_{max.}$ (CCl_4) [6,7] 3 622.4 cm^{-1} with $\Delta\nu_{1/2}$ 18.2 cm^{-1} and α : β 0.78; δ($CDCl_3$) 3.75 (3 H, s, OMe), 6.60 (1 H, bs, 8-H), 6.71 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.01 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 77.5; H, 8.75. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%).

(*b*) A solution of 7-methoxy-1,2,3,4,9,10-hexahydrophenanthren-2-ol (460 mg, 2.0 mmol) in dry alcohol (30 ml) was hydrogenated in the presence of 10% palladium–charcoal (180 mg) at room temperature and atmospheric pressure. After one hour the hydrogenation was complete. The catalyst was filtered off and the solvent was removed under reduced pressure. The oily residue was purified by preparative t.l.c. [benzene–ethyl acetate (4 : 1) with double development], giving the 2β-alcohol (9) (257.6 mg, 55.5%) and the 2α-alcohol (17) (70.9 mg, 15.3%), identical with the samples obtained in (*a*).

Sodium–Ammonia Reduction of 7-*Methoxy*-1,2,3,4,9,10-*hexahydrophenanthren*-2-*ol*.—Sodium metal (1.1 g, 47.8 mg-atom) was added to a solution of 7-methoxy-1,2,3,4,9,10-hexahydrophenanthren-2-ol (1.17 g, 5.1 mmol) in aniline (30 ml) and liquid ammonia (300 ml). The blue coloured solution was stirred for 0.5 h and then solid ammonium chloride (2.5 g) was added in portions to discharge the blue colour. The ammonia was evaporated off and water was added to the residue. Extraction with dichloromethane followed by usual work-up gave an oily residue which was purified by preparative t.l.c. [benzene–ethyl acetate (4 : 1) with double development], yielding 7-*methoxy*-1,2,3,4,4aα,9,10,10aβ-*octahydrophenanthren*-2α-*ol* (4) (696.6 mg, 59.0%), m.p. 94—97 °C (dichloromethane–ether) and its epimer (9) (41.7 mg, 3.5%), m.p. 75—80 °C, identical with that obtained from above experiments. The major product was recrystallized from the same solvent to provide an analytical specimen, m.p. 101—103 °C, $\nu_{max.}$ (CCl_4) [6,7] 3 622.7 cm^{-1} with $\Delta\nu_{1/2}$ 17.6 cm^{-1} and α : β 0.75; δ($CDCl_3$) 3.76 (3 H, s, OMe), 6.63 (1 H, bs, 8-H), 6.71 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.19 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 77.55; H, 8.7. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%).

7-*Methoxy*-1,2,3,4,4aα,9,10,10aβ-*octahydrophenanthrene* (3).—Alcohol (4) (480 mg, 2.07 mmol) was treated with toluene-*p*-sulphonyl chloride (480 mg) in dry pyridine (4 ml) and left at room temperature for 1 h. The mixture was quenched with ice–water and extracted with dichloromethane. Usual work-up yielded a crystalline residue which was recrystallized from dichloromethane–ether to give the corresponding tosylate (621.6 mg, 77.9%), m.p. 151—152 °C. The crystalline tosylate (200 mg, 0.518 mmol) was dissolved in dry tetrahydrofuran (20 ml) and then lithium aluminium hydride (200 mg) was carefully added. The resultant mixture was gently refluxed for 6 h. Extraction with dichloromethane followed by usual work-up left an oily residue which was purified by fractional distillation to give the pure *octahydrophenanthrene* (3) (93.6 mg, 83.6%), b.p. 128—129 °C/1 mmHg, δ($CDCl_3$) 3.74 (3 H, s, OMe), 6.60 (1 H, bs, 8-H), 6.70 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.18 (1 H, d, *J* 8 Hz, 5-H, (Found: C, 83.15; H, 9.35. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

7-*Methoxy*-1,2,3,4,4aα,9,10,10aα-*octahydrophenanthrene* (15).—Boron trifluoride–ether (3 ml) was added dropwise to a stirred ice-cold solution of the phenanthrenone (16) (3 g, 13.0 mmol) in ethane-1,2-dithiol (6 ml). The solution was left at room temperature for 16 h and then poured into cold aqueous sodium hydroxide. Extraction with dichloromethane followed by usual work-up left an oily residue which afforded, on crystallization from dichloromethane–ether, the corresponding ethylene dithioacetal (3.63 g, 90.9%), m.p. 104—106 °C. The crystalline thioacetal (1.25 g, 4.08 mmol) was dissolved in dry methanol–dioxan (1 : 1) (150 ml). The resulting solution was refluxed with w-2 Raney nickel (*ca.* 20 g) under vigorous stirring for 5 h. The catalyst was filtered off and the solvent was removed under reduced pressure. The resultant oily product was purified by fractional distillation to furnish the pure *octahydrophenanthrene* (15) (616.4 mg, 69.8%), b.p. 105—108 °C/0.5—0.6 mmHg, $\lambda_{max.}$ (EtOH) 279 and 287.5 nm (ε 2 200 and 2 050); δ($CDCl_3$) 3.75 (3 H, s, OMe), 6.60 (1 H, bs, 8-H), 6.73 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.01 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 83.45; H, 9.3. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

7-*Methoxy*-2-*methyl*-1,2,3,4,4aα,9,10,10aα-*octahydrophenanthren*-2-*ols* (10) *and* (18).—To a stirred solution of phenanthrenone (16) (1 g, 4.34 mmol) in dry tetrahydrofuran–ether (1 : 2) (24 ml), was added dropwise 2.30M-ethereal methylmagnesium iodide solution (6 ml, 13.8 mmol) under nitrogen with ice-cooling. The mixture was stirred at room temperature for 1 h, then refluxed for 1 h, and poured into cold aqueous ammonium chloride. Extraction with ether–dichloromethane (3 : 1) followed by usual work-up gave an oily residue which was purified by preparative t.l.c. [cyclohexane–ethyl acetate (2 : 1) with double development], affording the 2β-*alcohol* (18) (419.4 mg, 39.2%), m.p. 111—113 °C (pentane) and the 2α-*alcohol* (10) (252.0 mg, 23.5%), m.p. 74—78 °C (pentane). Recrystallization from ether–pentane furnished both analytical samples. The 2β-alcohol (18) had m.p. 113—114 °C, δ($CDCl_3$) 1.23 (3 H, s, 2-Me), 3.74 (3 H, s, OMe), 6.61 (1 H, bs, 8-H), 6.72 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.08 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 78.05; H, 9.1. $C_{16}H_{22}O_2$ requires C, 78.01; H, 9.00%). The 2α-alcohol (10) had m.p. 78—80 °C, δ($CDCl_3$) 1.13 (3 H, s, 2-Me), 3.76 (3 H, s, OMe), 6.63 (1 H, bs, 8-H), 6.74 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.22 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 77.85; H, 9.15. $C_{16}H_{22}O_2$ requires C, 78.01; H, 9.00%).

7-Methoxy-2-t-butyl-1,2,3,4,4aα,9,10,10aα-octahydrophenanthren-2-ols (11) *and* (19).—To a Grignard solution prepared from magnesium (3 g, 0.123 g-atom), t-butyl chloride (12 g, 0.13 mol), and dry ether (60 ml), was added slowly a cold solution of the phenanthrenone (16) (3 g, 0.013 mol) in dry benzene (60 ml). The mixture was stirred at room temperature overnight and then refluxed for 2 h, poured into aqueous ammonium chloride and extracted with ether–dichloromethane (3 : 1). The extract was usually worked up to leave an oily residue which was purified by preparative t.l.c. [cyclohexane–ethyl acetate (4 : 1) with double development], giving the 2β-*alcohol* (19) (547.2 mg, 14.6%), m.p. 97—100 °C (pentane) and the 2α-*alcohol* (11) (135 mg, 3.6%), m.p. 83—85 °C (pentane). Both analytical specimens were obtained by recrystallization from ether–pentane. The 2β-alcohol (19) had m.p. 100—102 °C, δ($CDCl_3$) 0.93 (9 H, s, 2-Bu^t), 3.75 (3 H, s, OMe), 6.60 (1 H, bs, 8-H), 6.71 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.02 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 79.35; H, 9.95. $C_{19}H_{28}O_2$ requires C, 79.12; H, 9.79%). The 2α-alcohol (11) had m.p. 86—87 °C, δ($CDCl_3$) 0.80 (9 H, s, 2-Bu^t), 3.77 (3 H, s, OMe), 6.63 (1 H, bs, 8-H), 6.73 (1 H, dd, *J* 2.5 and 8 Hz, 6-H), and 7.23 (1 H, d, *J* 8 Hz, 5-H) (Found: C, 78.95; H, 9.9. $C_{19}H_{28}O_2$ requires C, 79.12; H, 9.79%).

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