in dry pyridine (6 mL) was added. The reaction mixture was placed in the dark at ambient temperature (ca. 25 °C) for 24 h. A solution of sodium bisulfite (1.2 g) in water (20 mL) and pyridine (15 mL) was added, and the resultant mixture was stirred vigorously at ambient temperature for 2 h and then extracted with $CHCl_3$ (8 × 20 mL). The $CHCl_3$ extracts were washed with 0.5 N HCl (3 × 33 mL), saturated sodium bicarbonate solution (25 mL) and brine (2 × 25 mL), dried (Na_2SO_4), and concentrated to give an oil (0.571 g). Chromatography of the crude product on silica gel (50 g) with ethyl acetate/hexane (1:4) as the eluent afforded diol **12** (0.401 g, 71%) as a white solid. Recrystallization of the solid from hexane/ether afforded white needles, mp 122–123 °C: IR (KBr) 3340, 2940, 980, 760, 740 cm^{-1}; ^1H NMR δ 7.4–7.0 (m, 4 H, aromatic), 4.6–4.1 (q, J = 6 Hz, 1 H, CH_3CHOH–), 3.1–1.1 (m, 14 H), 2.37 (br s, D_2O exchangeable, 2 H, glycol H), 1.32 (s, 3 H, C-4a-CH_3); MS, m/z 242 (M − 18), 131 (base).

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.09; H, 9.50.

1β-Acetyl-4aβ-methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol (11). Diol **12** (0.244 g, 0.94 mM) was dissolved in acetone (30 mL) and cooled to 0 °C. Jones reagent (0.23 mL, 0.61 mequiv) was slowly added in a dropwise manner until TLC (ethyl acetate/hexane, 2:3) indicated that little diol remained (ca. 1 h). Isopropyl alcohol (1 mL) was added, and the organic phase was decanted from the chromium salts. The salts were extracted with ether (3 × 10 mL), and the organic phases were combined, dried (Na_2SO_4), and concentrated to afford an oil (0.203 g). Chromatography on silica gel with ethyl acetate/hexane (3:7) as the eluent afforded hydroxy ketone **11** (0.056 g, 23%) as a white solid, mp 130–132 °C: IR (KBr) 3420, 2940, 1695, 760, 740 cm^{-1}; ^1H NMR δ 7.6–6.8 (m, 4 H, aromatic H), 3.09–1.1 (m, 12 H), 2.23 (s, 3 H, CH_3CO–), 1.00 (s, 3 H, C-4a-CH_3).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.81; H, 8.31.

The method of Omura and Swern was used.[6] A stock solution of 1.4 g (0.011 mol) of oxalyl chloride and 1.9 g (0.024 mol) of dimethyl sulfoxide in 30 mL of methylene chloride was prepared and maintained at −60 °C in a dry ice–chloroform bath. To 1.63 mL of that solution maintained at −60 °C was added slowly 0.130 g (0.5 mmol) of diol **12** in 1.0 mL of methylene chloride. After the addition was complete, the reaction mixture was stirred for 25 min and 0.24 mL (2.4 m mol) of triethylamine was added dropwise. After addition was complete, the cooling bath was removed, and water (3.0 mL) was added. Stirring was continued for 30 min, the organic layer was separated, the water layer was re-extracted with methylene chloride (2 × 3 mL), and the organic extracts were combined, dried (Na_2SO_4), and evaporated. Chromatography of the residue on 30 g of silica gel 60 with hexane–ethylacetate mixtures as eluent provided 0.050 g of hydroxy ketone **11** and 0.070 g of recovered diol **12**; yield, 84% based on recovered diol **12**.

1β-Acetyl-4aβ-methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol, Methanesulfonate Ester (9). Hydroxy ketone **11** (0.060 g, 0.23 mM) was dissolved in dry pyridine (4 mL), and methanesulfonyl chloride (0.0798 g, 0.7 mM) was added in a dropwise manner. This sat in the dark at 5 °C for 42 h before addition of ice-cold water (4 mL). The aqueous phase was extracted with $CHCl_3$ (5 × 5 mL). The organic phase was washed with brine (5 mL), ice-cold 1 N H_2SO_4 (10 mL), and brine (5 mL), dried (Na_2SO_4), and concentrated to give an oil (0.59 g). ^1H NMR indicated an incomplete reaction, so this material was redissolved in pyridine (4 mL), and methanesulfonyl chloride (0.0798 g, 0.7 mM) was again added. The reaction mixture sat at 5 °C for 12 h and then at ambient temperature for 26 h. An identical workup as before afforded **9** as a brown oil. The reaction mixture was used in the subsequent Favorskii reaction without any further purification: ^1H NMR δ 7.4–7.0 (m, 4 H), 3.1 (s, 3 H, $-SO_2CH_3$), 3.0–1.2 (m, 11 H), 2.23 (s, 3 H, $-COCH_3$), 1.0 (s, 3 H, C-4a-CH_3).

Methyl 1β,4aβ-Dimethyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1α-carboxylate (10). The method of House and Gilmore was used.[3] A 0.0012 mol/mL solution of sodium methoxide in dimethoxyethane (DME) was prepared by dissolving sodium (0.132 g, 0.0057 g-atom) in methanol (2 mL) and adding dry DME (46 mL). To this NaOMe solution (7 mL, 0.84 mM) was added a solution of mesylate **9** (0.0693 g, 0.21 mM) in dry DME (2 mL). The reaction mixture was then stirred at ambient temperature under argon for 3 h while it was monitored by TLC. After an additional 8 h, TLC showed no further change, so the reaction was worked up by addition of H_2O (7 mL) and extraction with ether (7 × 5 mL). The ether layers were dried (Na_2SO_4) and concentrated to afford a brown oil (0.0219 g). The aqueous phase was acidified to ca. pH 2 with cold 6 N H_2SO_4 and extracted with ether (5 × 5 mL). The ether layers were dried (Na_2SO_4) and concentrated to afford an oil (0.0074 g) whose TLC (ethyl acetate/hexane, 1:4) was the same as above. The oils were combined and preparative TLC afforded **10** as a solid, mp 111–112 °C (lit.[11] mp 114–115 °C): IR ($CHCl_3$) 2950, 1740, 760, 740 cm^{-1}; ^1H NMR δ 7.26–7.04 (m, 4 H), 3.67 (s, 3 H, OCH_3), 3.0–1.3 (m, 11 H), 1.28 (s, 3 H, C-1-CH_3), 1.22 (s, 3 H, C-4a-CH_3); MS, m/z 272 (M^+), 257 (M − 15), 197 (base).

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Stereoselective Synthesis of 4a-Methyloctahydrophenanthrenes: A Novel Approach. 2. C-1 Substituted Series

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We report the stereoselective conversion of 4a-methyl-2,4a,9,10-tetrahydrophenanthrene (**1**), readily available from phenanthrene by reductive alkylation, via 4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene (**2**), into several C-1 substituted compounds. Chemical verification of stereochemistry is accomplished and the proton magnetic resonance characteristics of the substance are presented and discussed.

Continuing our studies of the preferred conformations of monosubstituted 4a-methyloctahydrophenanthrenes in solution,[1] we have now completed the stereospecific syntheses of all the possible C-1 4a-methyloctahydrophenanthrene isomeric amines and alcohols. In the present discussion the terms *cis* and *trans* will refer only to the A/B juncture; cis, 10aβ-H; trans, 10aα-H. The strategy for the proposed synthesis is shown in Scheme I and implies the preparation of the monoolefin, 4a-methyl-

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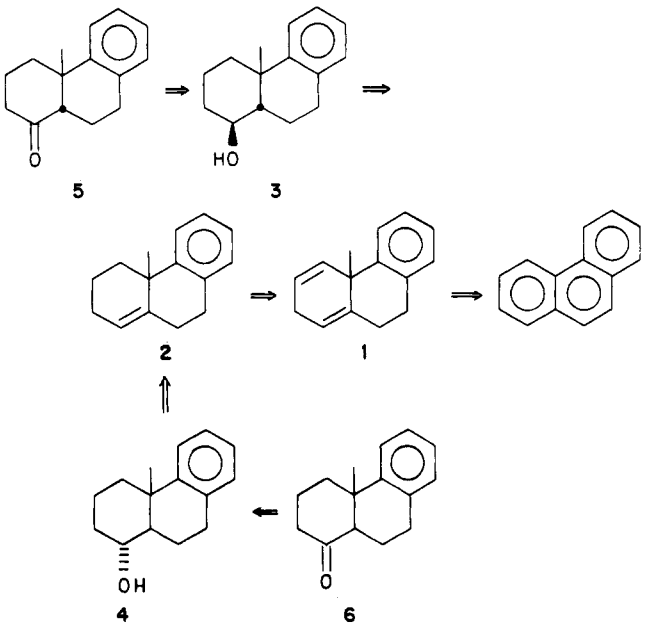
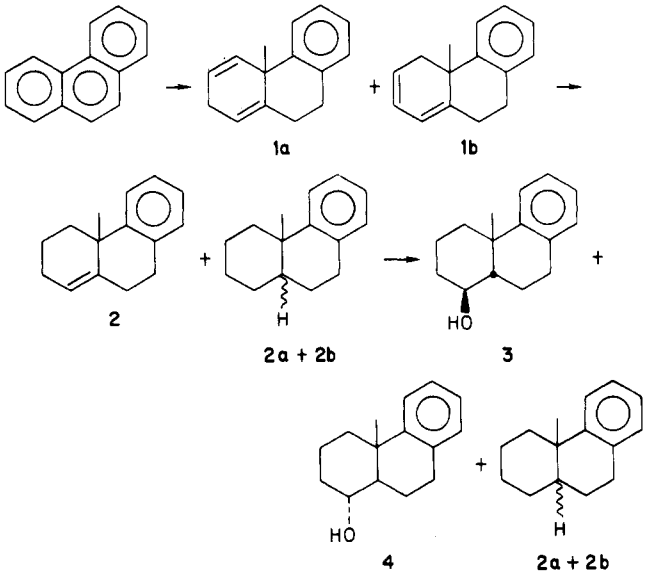
Scheme I



Scheme II



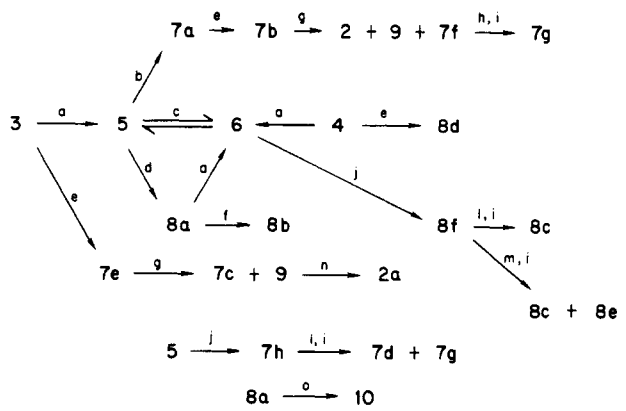
2,3,4,4a,9,10-hexahydrophenanthrene (**2**) by selective reduction of compound **1**, easily prepared from phenanthrene.[2,3]

The most critical step in this stategy would be the stereospecific formation of alcohols **3** and **4**. We felt that such stereoselectivity would be achieved by a hydroboration–oxidation[4a] reaction of olefin **2**. Oxidation followed by reductive amination[4b] of the resulting ketones **5** and **6** would provide the avenue to the nitrogen containing compounds.

Results and Discussion

The reductive alkylation of phenanthrene[2,3] with lithium in liquid ammonia produced dienes **1a** and **1b** (Scheme II) (95:5) in better than 95% yield. The crude mixture was then reduced over 10% palladium on charcoal reaction with hydrogen (40 psi) to produce a mixture of the desired olefin **2** (70%) plus a (3:1) mixture of **2a** and **2b**, the overreduced *cis*- and *trans*-4a-methyloctahydrophenanthrenes. Attempts to control over reduction by monitoring the hydrogen uptake were unsuccessful, and the use of more specific reagents,[5,6] such as (triphenylphosphine)rhodium chloride, was considered unnecessarily expensive in this case, since the following step, the hydroboration–oxidation, could be performed directly on the crude hydrogenation mixture. Hydroboration, utilizing diborane in THF, produced alcohols **3** and **4** in an 80:20 ratio, as shown by GLC analysis. Alcohol **3** could be isolated as a pure solid by fractional crystallization of the mixture after fast column separation of the nonpolar hydrocarbon impurities. In turn alcohol **4** was isolated from the mother liquor by preparative HPLC.

Scheme III[a]



[a] (a) CrO_3/H_2SO_4/acetone; (b) H_2/PtO_2/ethanol; (c) H^+ or OH^-; (d) H_2/PtO_2/3% KOH, ethanol; (e) TsCl/pyridine; (f) MsCl/pyridine; (g) KN_3/dimethylformamide; (h) $LiAlH_4$/ether; (i) 90% HCO_2H/37% HCHO/Δ; (j) $NH_2OH \cdot HCl$/NaOH/ethanol/Δ; (l) H_2/Raney nickel/ethanol; (m) sodium/ethanol; (n) H_2/10% palladium/charcoal/ethyl acetate; (o) lead tetraacetate/iodine/benzene.

Jones oxidation of alcohol **3** (Scheme III) produced ketone **5** which underwent reduction under neutral conditions with hydrogen over platinum oxide in ethanol giving mainly alcohol **7a** as a crystalline solid from cyclohexane. Ketone **5** readily isomerizes to ketone **6** and soon equilibrates to a 6 to 4 mixture of **5** and **6**. Equilibration is facilitated by either acid or base catalysis. The hydrogenation of ketone **5** or a mixture of **5** and **6** under basic conditions produced almost exclusively alcohol **8a**. Such results would seem to indicate that the reduction probably occurs in the ketonic rather than the enolic form. Thus, in the absence of the catalyst ketone **5**, due to the cis A/B ring function, will be reduced mainly from the more accessible β face, producing the α-alcohol. On the other hand, the presence of a basic catalyst produces an equilibrium mixture of the two ketones, and as the reduction of **6**, possessing a trans A/B ring junction, may be faster than reduction of **5**, and as reduction should occur exclusively from the less hindered α-face, it will yield alcohol **8a**.

Since all the attempts to introduce the *N,N*-dimethylamino group by direct reductive amination[4b] of ketones **5** and **6** were unsuccessful, we decided to try azide displacement[7] of the alcohol tosylates. Unfortunately the same steric features that caused the failure of direct amination acted on the displacement reaction causing the

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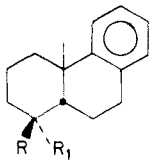
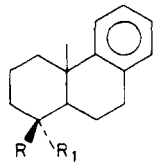
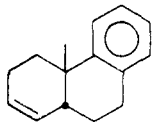


7a, R = H; R_1 = OH
b, R = H; R_1 = OTs
c, R = H; R_1 = N_3
d, R = H; R_1 = $N(CH_3)_2$
e, R = OTs; R_1 = H
f, R = N_3; R = H
g, R = $N(CH_3)_2$; R_1 = H
h, R = R_1 = oxime

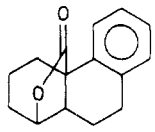


8a, R = OH; R_1 = H
b, R = OMs; R_1 = H
c, R = $N(CH_3)_2$; R_1 = H
d, R = H; R_1 = OTs
e, R = H; R_1 = $N(CH_3)_2$
f R = R_1 = oxime

competitive E2 reaction to become the predominant one. Thus, when submitted to the conditions described by Bose et al.,[8] only minor quantities (<8%) of the cis azides **7c** and **7f** were obtained, together with olefins **2** and **9**. Although from a synthetic point of view the displacement reaction had to be discarded, the transformation of azide **7f** into the corresponding amine allowed us to establish firmly the stereochemistry of amines **7d** and **7g**. Furthermore, the analysis of the reduction products of olefin **9** provided proof of the cis A/B junction for ketone **5**.



9



10

The *N,N*-dimethylamines were ultimately prepared by reduction followed by methylation of the oximes obtained from ketones **5** and **6**. The cis (**7h**) and trans (**8f**) oximes were easily separated by column chromatography so, although some isomerization occurred during the oxime formation, pure oximes could be obtained prior to the reduction step. Fortunately, in spite of the facile equilibration of ketones **5** and **6**, oxime formation carried out under drastic basic conditions[16] produced little isomerization, and when done with freshly prepared ketone, the major oxime in the mixture (usually more than 90%) could be isolated pure by simple recrystallization. Catalytic reduction (Raney nickel) of the cis oxime **7h**, followed by formic acid–formaldehyde *N,N*-dimethylation, gave mixtures of the β (**7g**) and α (**7d**) isomers in a ratio of 3:1. Only the β isomer could be isolated in pure form.

The trans oxime **8f** yielded mainly the β isomer **8c** when hydrogenated over platinum oxide and produced a mixture of both epimers in a ratio α:β of 82:18 when reduced with sodium in ethanol. Both trans isomers could be separated in pure form by column chromatography.

Assignment of Stereochemistry

The assignment of stereochemistry of the different products was made on the basis of chemical and spectroscopic (^{1}H NMR) evidence.

Alcohol **8a** was confirmed to be the 10aα, 1β-OH by the observations that when **8a** was submitted to oxidation with lead tetraacetate and iodine,[9] it produced lactone **10**. This type of intramolecular free radical hydrogen transfer reaction is extremely dependent on stereochemistry, and it requires the reactive sites to be close enough to allow the extraction of the hydrogen radical. Besides, the transfer step is highly favored by the possibility of a six-membered cyclic transition state.[10] In our situation a trans A/B ring junction and a C1, β-OH orientation will meet all of these requirements. This is in agreement with the small width of half-height ($w_{1/2}$) value for the C1-H, an equatorial proton, and with the difficulty to form the tosylate of **8a** and the instability of its mesylate **8b**.

The stereochemistry of the remaining alcohols could be determined relative to alcohol **8a** as follows: alcohols **8a** and **4** both produce the same ketone **6** upon Jones oxidation which means that alcohol **4** is the C-1 epimer of **8a**, that is, the C-1, α-OH isomer. This is in complete agreement with a $w_{1/2}$ value (26 Hz) for its C-1-methine hydrogen which is consistent with an axial hydrogen. Alcohol **4** is produced together with alcohol **3** from a common intermediate through a hydroboration–oxidation sequence. As the hydroboration–oxidation sequence is well established to produce cis hydroxyl and hydrogen addition, it follows that alcohol **3** must have the C-10a, β-H and C-1, β-OH. In addition, the tosylate **7e** of alcohol **3** produces only one elimination product: olefin **9**, which when submitted to catalytic hydrogenation gives exclusively hydrocarbon **2a**, a known 4a-methyloctahydrophenanthrene possessing a cis A/B ring juncture.[2] Alcohol **7a**, the remaining alcohol of the series, must therefore have the C-10a, β-H and C-1, α-OH configuration. This was confirmed by its oxidation to ketone **5** and its conversion, via the tosylate **7b** and attempted azide displacement to a mixture of azide **7f** and olefins **2** and **9**. Finally analysis of its ^{1}H NMR characteristics (see below) supported this assignment of stereochemistry.

The stereochemistry of the *N,N*-dimethylamine derivatives was assigned separately for the trans and the cis series. The C-1, β-$N(CH_3)_2$ axial configuration was assigned to compound **8c** on the following evidence. It was nearly the exclusive product produced when oxime **8f** was reduced catalytically and the resultant amine methylated. Since it is well-known that a trans A/B juncture favors the uptake of hydrogen from the α face when there is a substituent greater than H at C-4a, **8c** as the predominant product should be C-1-β. Besides the ^{1}H NMR signal for the C-4a-methyl is in agreement[1] with that expected for a compound possessing a strong 1–3 diaxial interaction between the methyl and an axial *N,N*-dimethylamino group. In addition when the reduction of oxime **8f** was carried out with sodium in ethanol and the resultant amines were methylated, the major product was isomer **8e** as expected since such a reduction should favor production of an equatorial product.

In the cis series, the C-1, β-$N(CH_3)_2$ configuration was assigned to compound **7g** by direct comparison with the amine synthesized from azide **7f**, which in turn was obtained from alcohol **7a** through a displacement reaction of the corresponding tosylate **7b**. Such azide displacements involve an inversion of configuration.

^{1}H NMR Spectral Characteristics

As we have discussed previously, the chemical shift of the C-4a methyl in the ^{1}H NMR in 4a-methyloctahydrophenanthrenes is extremely sensitive to conformational and configurational changes.[1,11] There is a clear relationship between the chemical shift of the methyl group and the value of the dihedral angle, A, subtended by the plane of the aromatic ring extended through the C-4a to C-4b bond and the C-4a to methyl carbon bond at C-4a. The ^{1}H NMR chemical shifts of the C-4a-methyl and

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Table I. C-10aα Series

compd	R_1	R_2	δ C-1-H (ppm)	$w_{1/2}$ (Hz)	δ C-4a-CH_3 (ppm)	$\Delta\delta^a$	$N(CH_3)_2$ (ppm)
2b	H	H			1.07		
4	H	OH	3.56	26	1.08	(+0.01)	
8d	H	OTs	4.64	26	1.09	(+0.02)	
8e	H	$N(CH_3)_2$			1.10	(+0.03)	2.30
8a	OH	H	4.01	6	1.42	(+0.35)	
8b	OMs	H	4.92	6	1.26	(+0.19)	
8c	$N(CH_3)_2$	H			1.46	(+0.39)	2.23
6	C-1 oxo				1.01		
8f	C-1 oxime				1.06		

[a] $\Delta\delta$ = (δ C-4a-CH_3)$_{substituted}$ − (δ C-4a-CH_3)$_{hydrocarbon\ 2b}$.

Table II. C-10aβ Series

compd	R_1	R_2	δ C-1-H (ppm)	$w_{1/2}$ (Hz)	δ C-4a-CH_3 (ppm)	$\Delta\delta$	$N(CH_3)_2$ (ppm)
2a	H	H			1.23		
7a	H	OH	4.23	18	1.38	(+0.15)	
7b	H	OTs	4.90	18	1.27	(+0.04)	
7c	H	N_3			1.35	(+0.12)	
7d	H	$N(CH_3)_2$			1.38	(+0.15)	2.25
3	OH	H	3.36	22	1.20	(−0.03)	
7e	OTs	H	4.40	20	1.13	(−0.10)	
7f	N_3	H			1.21	(−0.02)	
7g	$N(CH_3)_2$	H			1.20	(−0.03)	2.20
5	C-1 oxo				1.38		
7h	C-1 oxime				1.36		

C-1-H for the trans (C-10a-αH) compounds are listed in Table I. The values of $w_{1/2}$ for the C-1-H are also reported. Inspection of Table I reveals that the chemical shifts of the 4a-methyl of the C-1α-substituted compounds differ very little (less than 0.04 ppm) from the δ value of the unsubstituted hydrocarbon **2b**, while the C-4a-methyl signals for the C-1-β-isomers are substantially (Δβ: 0.23–0.19 ppm) shifted downfield. This difference is consistent with that found for the C-3-substituted series[1] and cannot be attributed to conformational differences (changes in angle A). The trans A/B ring juncture is rigid and the $w_{1/2}$ values of ca 6 Hz for the C-1-αH suggest that ring A maintains a chair conformation.[12] Therefore, the deshielding of the C-4a-methyl must be due to a kind of electronic effect induced by the 1,3-diaxial interaction with the C-1 axial substituents. A comparison of the chemical shift values of the C-4a-methyl for the C-1-*N*,N-dimethylamines allows us to assign the C-1-α configuration to compound **8e** and the C-1-β to compound **8c**.

In Table II are the chemical shift values for the C-4a-methyl and the C-1-H for the cis (C-10a-βH) compounds. Also the $w_{1/2}$ values for the C-1-H are listed. In this particular instance there is no rigidity of the ring system so that configurational changes may produce variations in the conformation of the system and, consequently, changes in the values of angle A. Therefore, compounds in this series will exist as equilibrium mixtures of both extreme conformations: 98° < angle A < 135°. Thus for the unsubstituted hydrocarbon, **2a**, we would expect the chemical shift of the C-4a-methyl to lie at the average (more or less) of the extremes 1.07 and 1.38 ppm, as it does.

The effects of C-1-substituents can be observed in Table II. As in the C-3-substituted series,[1] the most noticeable features are the large C-1-H $w_{1/2}$ values (18–22 Hz), which mean that the C-1-substituents assume equatorial positions and, therefore, the variations of chemical shift of the C-4a-methyl must be due exclusively to changes in the population of conformers between the two extreme conformations. The C-1-α-substituted compounds will prefer conformations of greater values of angle A, thereby causing a downfield shift (+0.15 ppm) of the chemical shift of the C-4a-methyl. In contrast, β-substituents will favor those conformations with A values close to 98°, thus moving the C-4a-methyl out of the deshielding area of the aromatic ring. The fact that the values of chemical shift for the C-4a-methyl for this series do not depart markedly from that of the unsubstituted hydrocarbon ($\Delta\delta$ = 0.03 ppm) can be explained by considering that C-1-β substitution will displace the chemical shift of the angular methyl group of the more deshielded conformation (angle A = 135°) up to +0.40 ppm further downfield due to the additional 1,3-diaxial interaction introduced by the β-axial substituent. Therefore, the midpoint between the extreme conformations in this series is close to 1.40 ppm instead of 1.23 ppm. The observed δ's are therefore consistent with the C-1-β substituted compounds assuming preferred conformations with the substituent equitorial. As happens in the case of the trans isomers, a comparison of the C-4a-methyl chemical shift values of the cis C-1-*N*,*N*-dimethylamine substituted compounds clearly indicates that **7g** has the C-1-β configuration, while compound **7d** is the C-1-α isomer, in agreement with the assignments made through chemical correlation.

Experimental Section

All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-33, Perkin Elmer 257, or Perkin-Elmer 281B spectrometer as 1% KBr pellets or as films between NaCl plates. ^{1}H NMR spectra were obtained with a Varian Associates EM-360 or a JEOL-C-60HL spectrometer. FT ^{1}H NMR spectra were obtained in a JEOL-C-FX60 spectrometer. All the ^{1}H NMR spectra were obtained in $CDCl_3$ solution with Me_4Si as the internal standard unless stated otherwise. In ^{1}H NMR descriptions s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets. Mass spectra were recorded on a Varian Associates CH-5, DuPont Model 21-492 GC/MS, or Finnigan 3200F (GC/MS/DS) spectrometer. Microanalyses were performed on a Hewlett-Packard 185B CHN analyzer in the Department of Medicinal Chemistry, University of Kansas. Gas chromatographic analyses were conducted on a Varian Associates

(12) Jackman, L. M. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: New York, 1969; p 286.

Model 3700 or a Beckman GC-65 analytical gas chromatograph equipped with flame-ionization defectors and helium or nitrogen as carrier gas. HPLC was performed on a Waters Associates Model 660 solvent programmer equipped with a Model 440 absorbance detector. All the solvents used were distilled in glass prior to use. In the cases where anhydrous conditions were utilized, solvents were dried according to literature procedures, and the reactions were run in flame-dried apparatus under a positive pressure of argon or nitrogen atmosphere.

4a-Methyl-2,3,4,4a,9,10-hexahydrophenanthrene (2). 4a-Methyl-2,4a,9,10-tetrahydrophenanthrene, **1**, (30 g, 15.3 mM) obtained by the method of Campbell,[2] was dissolved in absolute ethanol (200 mL) and 10% Pd/C (4 g) was added. The mixture was hydrogenated at 25 °C and 20 psi until no further uptake of H_2 was observed (about 24 h). The catalyst was filtered and the ethanol was removed in vacuo to give 29.8 g of an oil. GC analysis (OV-17) of the crude oil showed it to be a mixture of the desired monoolefin **2** (60%) and the cis (30%) and trans (10%) hydrocarbons **2a** and **2b**. Pure **2** could be obtained by chromatography using 10% $AgNO_3$ impregnated silica gel with hexane as eluent, molecular distillation (0.020 mmHg, 50 °C): IR (neat) 2920, 1490, 1445, 760, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–6.81 (m, 4 H, Ar H), 5.38 (br, s, 1 H olefinic H), 2.9–2.6 (m, 2 H, benzylic H), 2.6–1.5 (m, 8 H, aliphatic), 1.35 (s, 3 H, C-4a-CH_3); MS, m/z (relative intensity) M^+, 198 (10.5), 183 (100), 155 (13.7), 141 (42), 129 (13), 128 (12), 115 (18).

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-1β-phenanthrol (3) and 4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol (4). The method of Zweifel and Brown[13] was used. Monoolefin **2**, (8 g, 0.404 mM) was dissolved in dry THF (25 mL) and cooled to 0 °C. Diborane (ca. 0.6 mol of BH_3) was generated in situ from BF_3–etherate and $NaBH_4$ as described[13] and was bubbled into the solution of monoolefin with a stream of dry nitrogen. The reaction mixture was then stirred at ca. 25 °C for 12 h. For workup, the mixture was cooled to 0 °C, and water was slowly added to react with excess diborane (caution), followed by slow simultaneous addition of 3 N NaOH (5 mL) and 30% H_2O_2 (5 mL), while stirring vigorously. During the addition the temperature must be kept below 40 °C. The reaction mixture was then treated at 40 °C for 2 h; after cooling, ether (50 mL) was added, and the organic phase was washed with saturated NaCl solution (20 mL), dried (Na_2SO_4), and concentrated in vacuo to afford 8.0 g of a colorless oil. GC analysis (2.4 m × 2 mm, glass, 3% Carbowax 20M, 70–190 °C, 3.5 °C/min, 30 cc/min N_2) of the crude oil showed it to be a mixture of the cis and trans hydrocarbons **2a** (23%) and **2b** (6%) and alcohols **3** and **4** (70%). Silica gel chromatography (800 g) with ether/hexane (30:70) as eluent gave a mixture of hydrocarbons (2.3 g, **2a**:**2b**, 3:1) and a mixture of alcohols **3** and **4** (5.06 g **3**:**4**, 9:1). Cis alcohol **3** could be obtained pure as a solid (4.03 g, mp 95–96 °C) by recrystallization of the mixture from hexane: IR (KBr) 3290, 2940, 760, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–6., (m, 4 H, aromatic H), 3.36 (m, 1 H, $w_{1/2}$ = 24 Hz, C*H*OH), 2.9–2.65 (m, 2 H, benzylic H), 2.3–1.2 (m, 10 H, aliphatic H), 1.20 (s, 3 H, C-4a-CH_3); MS, m/z M^+ 216, 198, 183 (base), 141.

Anal. Calcd for $C_{15}H_{20}O$: C, 83.23 H, 9.23. Found: C, 83.08; H, 9.48.

Alcohol **4** (0.186 g) was isolated in pure form from the mother liquors of recrystallization of **3** by HPLC of 0.230 g of the mixture using a silica gel column Whatman, Magnum 9 and 8% THF in hexane as eluent. Alcohol **4** is a colorless oil; IR (neat) 3300, 2940, 760, 740 cm^{-1}; ^1H NMR δ ($CDCl_3$) 7.4–6.8 (m, 4 H, aromatic H), 3.56 (m, 1 H, $w_{1/2}$ = 28 Hz C*H*OH), 3–2.5 (m, 2 H, benzylic H), 2.5–1.0 (m, 10 H, aliphatic H), 1.08 (s, 3 H, C-4a-CH_3).

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-1β-phenanthrol Tosylate (7e). Prepared as described by P. R. Schleyer[14] from alcohol **3** (0.67 g, 3.1 mM) in anhydrous pyridine (5 mL) cooled to 0 °C with the addition of TsCl (1.18 g, 6.2 mL). After 48 h at 0–5 °C the mixture was poured onto crushed ice (10 g), stirred for 30 min, extracted with ether (4 × 15 mL), washed with cold aqueous 10% HCl (1:1) and saturated brine, (2 × 10 mL), dried (Na_2SO_4), and evaporated, affording a colorless oil (1.0 g) recrystallized from hexane (0.977 g, 80%): mp 122–122.5 °C; ^1H NMR ($CDCl_3$) δ 7.7 (d, 2 H, J = 8 Hz, *o*-H Ar tosylate), 7.33–6.83 (m, 6 H, aromatic H), 4.36 (m, 1 H, $w_{1/2}$ = 20 Hz, *CHOTs*), 2.41 (s, 3 H, tosylate-CH_3), 1.26 (s, 3 H, C-4a-CH_3).

Anal. Calcd for $C_{22}H_{26}SO_3$: C, 71.32; H, 7.07. Found: C, 71.41; H, 7.13.

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol tosylate (8d) was prepared from alcohol **4** in 78% yield, as described for (**7e**), mp 127–128 °C from MeOH: ^1H NMR ($CDCl_3$) δ 7.83 (d, 2 H, J = 8 Hz, *o*-H Ar tosylate), 7.41–7.04 (m, 6 H, aromatic H), 4.64 (m, 1 H, $w_{1/2}$ = 26 Hz, -*CH*-OTs), 2.79 (m, 2 H, benzylic H), 2.46 (s, 3 H, tosylate-CH_3), 2.30–1.1 (m, 6 H, aliphatic), 1.08 (s, 3 H, C_{4a}-CH_3).

Anal. Calcd for $C_{22}H_{26}SO_3$: C, 71.32; H, 7.07. Found: C, 71.15; H, 7.27.

4a-Methyl-3,4,4a,9,10,10aβ-hexahydrophenanthren-1-(2*H*)-one (5). Jones reagent[15] was slowly added to a cooled (0°) solution of alcohol **3** (3.42 g, 15.47 mM) in acetone (30 mL). The reaction was stirred at 0 °C for 10 min. The excess of oxidant was consumed with isopropyl alcohol (1.0 mL), and anhydrous K_2CO_3 (2.0 g) was added. The acetone was decanted, and the cromium salts were washed with ether (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and decanted, and the solvent was eliminated in vacuo to afford a colorless oil, 3.01 g (91%): IR (neat) 1715 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.6–7.0 (m, 4 H, Ar H), 3.0–2.6 (m, 2 H, benzylic), 2.5–1.4 (m, 9 H, aliphatic), 1.38 (s, 3 H, CH_3), oxime, mp 134–135 °C (cyclohexane).

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-1α-phenanthrol (7a). Ketone **5** (1.0 g, 4.6 mM)in absolute EtOH (100 mL) and PtO_2 (0.150 g) was hydrogenated (50 psi of H_2) in a Parr series apparatus for 3 h. The catalyst was removed by filtration, and the solvent was evaporated in vacuo; the resulting colorless oil was crystallized from cyclohexane (0.630 g) as pure alcohol **7a**: mp 128–129 °C; IR (KBr) 3230 cm^{-1} (OH), ^1H NMR ($CDCl_3$) δ 7.33–6.9 (m, 4 H, Ar H), 4.23 (m, 1 H, $w_{1/2}$ = 18 Hz, C*H*OH), 3.0–2.7 (m, 2 H, benzylic), 1.40 (s, 3 H, C-4a-CH_3).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.51; H, 9.27.

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-1β-phenanthrol (8a). Ketone **5**, (1.75 g, 8.17 mM) in 3% ethanolic KOH (150 mL) and PtO_2 (0.200 g) was hydrogenated (30 psi) in a Parr series apparatus for 24 h. The catalyst was removed by filtration, and the solvent was removed in vacuo (40 °C); the residue was taken up in ether (50 mL), washed with saturated brine (2 × 20 mL), and dried (Na_2SO_4), and the solvent was eliminated in vacuo. The crude residue (1.66 g) was chromatographed on silica gel 60 (160 g), eluted with ether–hexane (20:80). Three fractions were collected from the residue: 0.160 g of hydrocarbon (**2a** + **2b**), 0.250 g of ketone mixture (**5** and **6**; 3:1), and 1.40 g (75%) of pure alcohol (**8a**). Alcohol **8a** is a very low melting solid; IR (film) 3300, 1028 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–6.83 (m, 4 H, Ar H), 3.95 (br t, 1 H, $w_{1/2}$ = 7 Hz, C*H*OH), 3.0–2.7 (m, 2 H, benzylic), 2.5–1.1 (m, 9 H, aliphatic), 1.28 (s, 3 H, C-4a-CH_3); MS, m/z 216 (M^+) 198, 183 (base peak).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.40; H, 9.17.

4a-Methyl-3,4,4a-9,10,10aα-hexahydro-1(2*H*)-phenanthrone (6) was prepared by the same procedure as used for formation of **5**. Alcohol **8a** (2.0 g, 9.34 mM) produced 1.807 g (90%) of ketone **6**, as a colorless oil (oxime, mp 190–191 °C from EtOH): IR (neat), 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–6.9 (m, 4 H, Ar H), 2.95–2.55 (m, 2 H, benzylic), 2.40–1.0 (m, 9 H, aliphatic), 1.05 (s, 3 H, C-4a-CH_3).

4a-Methyl-3,4,4a,9,10,10aβ-hexahydrophenanthren-1-(2*H*)-one Oxime (7h). To a cooled (0 °C) suspension of ketone **5** (1.70 g, 7.94 mM) freshly prepared from alcohol **3** and hydroxylamine hydrochloride (0.938 g, 13.5 mM) was added powdered NaOH (2.0 g, 50 mM) portion-wise while stirring vigorously.[16] After the addition was completed, the mixture was heated on a steam bath for 10 min, cooled, and poured into 100 mL of crushed ice–water. The resulting mixture was neutralized by

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careful addition of cold 2 N HCl, and the solid formed was collected by filtration. The crude product was dried, affording 1.78 g (98%) of an amorphous powder containing less than 10% of the 10aα isomer. Pure **7h** was obtained (77%) after recrystallization from cyclohexane, mp 134–135 °C: IR (KBr) 3250, 3070, 3030, 2950, 1500, 1470, 1450, 950, 930, 900, 755, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.90 (br s, 1 H, exchangeable with D_2O, =NOH), 7.33–6.83 (m, 4 H, Ar H), 3.30 (m, 1 H, C-10a-βH), 2.91 (m, 2 H, benzylic), 2.60–1.20 (m, 8 H, aliphatic), 1.36 (s, 3 H, C-4a-CH_3).

Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.58; H, 8.54; N, 5.92.

4a-Methyl-3,4,4a,9,10,10aα-hexahydrophenanthren-1-(2*H*)-one Oxime (8f). The same procedure as in **7h**, from freshly prepared **6** (1.0 g, 4.67 mM), yielded 0.938 (88%) of crude oximes; after one recrystallization from EtOH, pure **8f** (0.700 g) was obtained: mp 190–190.5 °C; IR (KBr) 3240, 3060, 3010, 2940, 2900, 2850, 1500, 1400, 980, 910, 760, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.66 (s, 1 H, exchangeable with D_2O =NOH), 7.60–6.87 (m, 4 H, Ar H), 3.38 (m, 1 H, C-10a-α-H), 2.82 (m, 2 H, benzylic), 2.68–1.20 (m, 8 H, aliphatic H), 1.06 (s, 3 H, C-4a-CH_3).

Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.85; H, 8.50; N, 5.89.

1β-(Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (7g). To oxime **7h** (1.0 g, 4.36 mM)in EtOH (30 mL) was added a teaspoon of Raney nickel freshly prepared,[17] and the mixture was hydrogenated on a Parr series apparatus (50 psi of H_2) for 24 h. The catalyst was filtered, and the solvent was eliminated in vacuo. The residue was partitioned between 1 N HCl (75 mL) and ether (2 × 30 mL). The aqueous layer was then made alkaline (pH 11) with NaOH and extracted with chloroform (2 × 20 mL). The combined chloroform extracts were dried over sodium sulfate, decanted, and evaporated. The residue (0.800 g) was dissolved in 90% formic acid (10 mL) 37% formaldehyde[18] in water (4.0 mL) was added, and the mixture was gently refluxed (8 h). The solvent was eliminated in vacuo, and the residue was taken up in 10% HCl (5.0 mL) and evaporated to dryness under reduced pressure. This process was repeated until no more formaldehyde could be detected. Finally the residue was taken up in 10% HCl (20 mL) and extracted with ether (3 × 15 mL), and the aqueous layer was alkalinized (pH 10) with NaOH, saturated with NaCl, and extracted with chloroform (3 × 20 mL) providing 0.820 g (77%) of a yellowish oil. Column chromatography on 100 g of silica gel 60 with $CHCl_3$:MeOH:NH_4OH (95:4:1) as eluent afforded 0.530 g of **7g** and 0.260 g of a 2:1 mixture of **7g** and **7d**. Molecular distillation gave pure **7g** (130 °C (0.010 mmHg)); IR (neat) 2815, 2790, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.0 (m, 4 H, Ar H), 2.9–2.4 (m, 2 H, benzylic), 2.2 (s, 6 H, $N(CH_3)_2$), 2.3–1.2 (m, 9 H, aliphatic H), 1.20 (s, 3 H, C-4a-CH_3); MS, m/z 243 (M^+), 228, 198, 84 (base peak). Picrate salt for analysis, yellow needles (H_2O) mp 173–174 °C.

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.83. Found: C, 58.60; H, 5.90; N, 11.60.

Mixture of **7g** and **7d**: ^1H NMR ($CDCl_3$) δ **7g**, 2.20 (s, 6 H, $N(CH_3)_2$), 1.20 (s, 3 H, C-4a-CH_3); **7d**, 2.25 (s, 6 H, $N(CH_3)_2$), 1.38 (s, 3 H, C-4a-CH_3).

1β-(Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (8c). The same procedure as in **7g** was used. Oxime **8f** (0.300 g, 1.3 mM) produced 0.252 g (80%). After column chromatography (as above) 0.230 of **8c** was obtained. Molecular distillation (110 °C (0.025 mmHg)) gave pure **8c**: IR (neat) 3050, 3010, 2930, 2860, 2810, 2760, 1485, 1450, 760, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–6.8 (m, 4 H, Ar H), 2.90–2.40 (m, 2 H, benzylic), 2.23 (s, 6 H, $N(CH_3)_2$), 2.40–1.1 (m, 9 H, aliphatic), 1.48 (s, 3 H, C-4a-CH_3); MS, m/z 243 (M^+), 228, 198, 84 (base peak). Picrate salt for analysis, yellow needles from H_2O mp 185–186 °C dec.

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.83. Found C, 58.56; H, 5.70, N, 11.80.

1α-(Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (8e). Oxime **8f** (0.243 g, 1.1 mL) was dissolved in absolute EtOH (5 mL), and sodium (0.230 g, 10 mL) was added in small portions while stirring vigorously, at such a rate as to maintain reflux. After all the sodium went into solution, the mixture was boiled for 10 additional min, the solvent was evaporated under reduced pressure, and the residue was partitioned between H_2O and chloroform (15 mL each). The $CHCl_3$ was decanted, and the aqueous phase was extracted with fresh chloroform (2 × 10 mL). The combined chloroform extracts were dried (Na_2SO_4) and evaporated to furnish 0.196 g of a yellow oil, which on treatment with formic acid/formaldehyde produced 0.176 g of the methylated amine mixture. Column chromatography (as above) gave 0.040 g of **8c** and 0.110 g (41%) of **8e**. Molecular distillation (60 °C (0.02 mm)) gave pure **8e**: IR (neat) 3060, 3010, 2960, 2925, 2820, 2780, 1485, 1450, 760, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.0 (m, 4 H, Ar H), 3.08–2.88 (m 2 H, benzylic H), 2.26 (s, 6 H, $N(CH_3)_2$), 2.05–1.20 (m, 9 H, aliphatic), 1.10 (s, 3 H, C-4a-CH_3); MS, m/z 243 (M^+), 228, 198, 84 (base peak).

Lactone 10. A mixture of alcohol **8a** (0.050 g, 0.23 mM), freshly recrystallized lead tetraacetate (0.307 g, 0.695 mM), and I_2 (0.176 g, 0.695 mM) in dry benzene (20 mL) was photolyzed under a 1000-W halogen lamp. After 1 h the reaction was complete (TLC showed disappearance of starting material), water (20 mL) was added, and the organic layer was decanted. The aqueous phase was extracted with ether (2 × 20 mL) and the combined organic extracts were washed with 10% aqueous sodium bisulfite solution, followed by water, dried over sodium sulfate, decanted, and evaporated to afford 0.053 g of a yellow oil. Column chromatography on silica gel (gradient of hexane–ether) gave 0.031 g of lactone **10**. Recystallization from hexane: mp 119–120 °C; IR (KBr) 3100, 3060, 3020, 2940, 2860, 1760, 1130, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.1 (m, 4 H, Ar H), 4.67 (br s, 1 H, $w_{1/2}$ = 6 Hz) CHOCO), 3.1–2.7 (m, 2 H, benzylic), 2.6–1.3 (m, 9 H, aliphatic); MS, m/z 228 (M^+) 198, 184, 141 (base peak), 128, 115, 77.

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthren-1β-ol Mesylate (8b). To alcohol **8a** (1.6 g, 7.4 mM) in dichloromethane (20 mL) was added triethylamine (1.2 g, 11.8 mM) and mesyl chloride (1.0 g, 7.6 mM) in dichloromethane (100 mL) over a period of 15 min. During the addition the mixture temperature was maintained at 10 °C. After the addition was complete, the mixture was stirred at 15 °C for 45 additional min, washed successively with cold (0 °C) water, 10% HCl, 2% sodium bicarbonate solution, and saturated brine, dried over sodium sulfate, decanted, and evaporated to dryness (40 °C) furnishing a yellow oil (1.5 g): ^1H NMR ($CDCl_3$) δ 7.4–6.8 (m, 4 H, Ar H), 4.9 (br s, 1 H, $w_{1/2}$ = 9 Hz, CHOMs) 3.07 (s, 3 H, SO_2CH_3), 2.62–1.5 (m, 11 H, benzylic + aliphatic H), 1.33 (s, 3 H, C-4a-CH_3). Compound **8b** is extremely unstable; any attempt of purification causes its decomposition, giving mainly olefin **2**.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthren-1α-ol Tosylate (7b). The same procedure as in **7e** from alcohol **7a** afforded tosylate **7b** in 88% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.71 (lower d of the AB quartet, 2 H), 7.4–6.73 (m, 6 H, Ar H), 4.9 (m, 1 H, $w_{1/2}$ = 20 Hz, CHOTs), 2.93–2.2 (m, 2 H, benzylic), 2.36 (s, 3 H, Ar CH_3), 2.15–1.2 (m, 9 H, aliphatic), 1.26 (s, 3 H, C-4a-CH_3).

1β-Azido-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (7f). The procedure of Campbell et al.[2] was used. Tosylate **7b** (0.277 g, 0.75 mM) was added in one portion to a preheated (80 °C) solution of potassium azide (0.304 g, 3.85 mM)in dimethylformamide (75 mL) and water (2.0 mL). After 2 h TLC analysis showed no change so the temperature was increased to 100 °C, and the mixture was stirred 3 more h whereupon TLC showed no more tosylate was present. The solvent was eliminated in vacuo, and the residue was taken up in chloroform (25 mL), washed with saturated brine, dried over sodium sulfate, decanted, and evaporated. The crude product was chromatographed on 27 g of silica gel 60 (hexane–EtOAc gradient) producing 0.110 g (82%) of olefin mixture (predominantly **2** but also containing (GC) some **9** and 0.013 g (7%) of azide **7f**): IR (neat) strong absorption 2095 cm^{-1}; ^1H NMR δ 7.40–6.9 (m, 4 H, Ar H), 3.2–2.5 (m, 3 H, benzylic + CHN_3), 2.3–1,2 (m, 9 H, aliphatic), 1.21 (s, 3 H, C-4a-CH_3).

1β-(Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (7g). The procedure of Micovic and Mihailovic was used.[19] Azide **7f** (~8 mg, 0.03 mM) in dry ether

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(5 mL) was added to a suspension of $LiAlH_4$ (10.0 mg, 0.26 mM) in dry ether (5 mL) and cooled to −78 °C with a dry ice–acetone bath. The mixture was stirred for 2 h and then allowed to warm up to 25 °C for 1 more h. The reaction was then successively treated with water (0.1 mL), 15% sodium hydroxide (0.1 mL), and the granular precipitate was filtered and washed with ether. The combined ethereal solutions were evaporated, and the residue was methylated as above producing a yellow oil (5.0 mg, 68%) identical (IR, ^1H NMR) with **7g** produced as above.

4a-Methyl-3,4,4a,9,10,10aβ-hexahydrophenanthrene (9) and 1α-Azido-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (7c). The same procedure was used as in **7f** starting with tosylate **7e** (0.280 g, 0.75 mL). A higher temperature (120 °C) was required to cause the disappearance of the starting tosylate. After workup and column chromatography, 0.120 g (80%) of olefin **9** and 0.013 g (7%) of azide **7c** were isolated.

Olefin 9: ^1H NMR ($CDCl_3$) δ 7.50–6.80 (m, 4 H, Ar H), 5.60 (br s, 2 H, olefinic H), 2.90–2.56 (m, 2 H, benzylic), 2.5–1.30 (m, 8 H, aliphatic), 1.32 (s, 3 H, C-4a-CH_3); MS, m/z 198 (M^+), 185, 183, 157, 141, 129 (bp), 115, 91, 77.

Azide 7c: IR 2095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H, C-4a-CH_3).

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (2a). Olefin **9** (0.1 g, 0.505 mmol) in (30 mL) was hydrogenated (30 psi H_2) in the presence of 10% Pd on charcoal (0.030 g) for 3 h. The catalyst was filtered, and the filtrate was concentrated in vacuo to yield 0.090 g (90%) of pure **2a** (GC). The ^1H NMR shows only one C-4a-CH_3 singlet for 3 H at δ ($CDCl_3$) 1.23 coincident with that reported by E. Wenkert and co-workers[11] for **2a**.

Registry No. 1, 22139-44-2; 2, 22139-45-3; **2a**, 79297-74-8; **2b**, 70561-39-6; 3, 98304-41-7; 4, 98330-23-5; 5, 98392-71-3; 6, 41487-66-5; **7a**, 98304-44-0; **7b**, 98304-54-2; **7c**, 98304-57-5; **7d**, 98304-50-8; **7e**, 98304-42-8; **7f**, 98304-55-3; **7g**, 98304-49-5; **7h**, 98304-46-2; **8a**, 98304-45-1; **8b**, 98304-53-1; **8c**, 98304-51-9; **8d**, 98304-43-9; **8e**, 98304-52-0; **8f**, 98304-47-3; 9, 98304-56-4; 10, 98330-24-6; 1β-amino-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene, 98304-48-4.

Aromatic Hydroxylation and Deacylation of 9-Acylanthracenes by Copper(II)–Peroxydisulfate[1]

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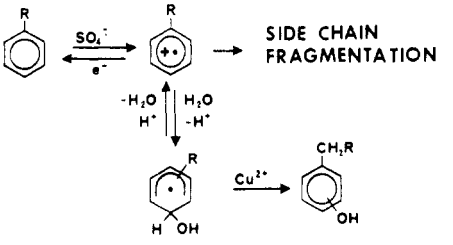
The Cu^{2+}–$S_2O_8^{2-}$ oxidations of 9-acylanthracenes (**1**) and 9-acyl-10-methylanthracenes (**10**) having formyl (**a**), acetyl (**b**), or benzoyl (**c**) groups were studied in refluxing acidic acetonitrile–water. Radical cations **1a–c**, **10a**, and **10c** reacted with water to produce 10-hydroxyl adduct radicals which were oxidized by Cu^{2+} to produce the corresponding hydroxylated products: 10-acylanthrols (**5**) from **1** and 9-acyl-10-methyl-9,10-dihydroxy-9,10-dihydroanthracenes (**15**) from **10**. Compounds **5** and **15** were unstable to reaction conditions and underwent subsequent reactions. Compound **5** underwent tautomerization competitive with oxidation to respectively produce 10-acyl-9-anthrones (**6**) and 10-acyl-10-hydroxy-9-anthrones (**8**). Compounds **6** and **8** were hydrolytically unstable, yielding respectively anthrone and 9,10-dihydroxyanthracene, at rates dependent on acidity (**6a**, **6b**, and **6c** exhibited 2.6, 44, and 45 min half-lives, respectively, in 0.1 M $HClO_4$). Compounds **15a** and **15c** solvolyzed in the acidic media to give 10-methylanthrol which was further oxidized to produce 10-methyl-10-hydroxy-9-anthrone (**12**). Partial dehydration of **12** produced 10-methylene-9-anthrone. Little product was formed by proton loss from the radical cations of **1a**, **10a**, and **10c**.

Aromatic hydroxylation and side chain oxidation reactions of aromatic compounds are known for peroxydisulfate oxidations.[2-8] These reactions are understood to derive from the reactions of initially formed radical cation intermediates. Attack by water and oxidation of the hydroxyl adduct radical by metal ion catalysts lead to the production of phenols (aromatic hydroxylation), whereas fragmentation of side chain functional groups to produce cations and radicals results in side chain oxidation products.

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}\cdot \quad (1)$$

$$Cu^{+} + S_2O_8^{2-} \rightarrow Cu^{2+} + SO_4^{-}\cdot + SO_4^{2-} \quad (2)$$



Most examples of these reactions have been provided by oxidation of monocyclic aromatic compounds with much emphasis on the study of functionalized alkyl side chain systems.[2-8] Few studies of $S_2O_8^{2-}$ oxidation of polycyclic aromatic compounds have been conducted. At least two studies of naphthalene oxidation have been reported,[9,10] but no oxidation of anthracenes are known. One reason for the limited study of polycyclic systems may be due to poor solubility in the aqueous medium normally employed for $S_2O_8^{2-}$ oxidations. Recent studies of peroxydisulfate oxidations of alkylaromatic compounds in

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