Stereoselective Synthesis of 4a-Methyloctahydrophenanthrenes: A Novel Approach. 1. C-2 and C-3 Substituted Series

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The regio- and stereoselective syntheses of variously C-2 and C-3 functionalized 4a-methyloctahydrophenanthrenes are described. The diene, 4a-methyl-$\Delta^{1(10a),3(4)}$-tetrahydrophenanthrene, is a key synthon and is readily prepared from phenanthrene. The chemical verification of stereochemistry is accomplished.

Although the preparation of the tricyclic 4a-methyloctahydrophenanthrene ring system present in numerous diterpene natural products has been accomplished in a variety of ways using a variety of methods,[1] none have provided ready access to materials regio- and stereoselectively functionalized in rings A or B without the presence of complicating functional groups elsewhere in the molecule. So that the conformational effects of groups might be analyzed as models for structure elucidation of naturally occurring ring A substituted diterpenes, we set about development of a procedure which would provide regio- and stereoselective functionalization of the ring positions of rings A and B. Introduction of stereochemically defined functionality into rings A or B of the octahydrophenanthrene ring system would also provide interesting compounds for evaluation for biological activity. In this paper we describe preparation of the series with substitutions at positions 2 and 3 in ring A.

Synthesis of Compounds

From an antithetic analysis, the various desired compounds of the C-2 substituted series would be readily available from the ketones **1** and **2**.[2] These ketones would be readily prepared by stereoselective reduction of the enone **3**. Enone **3** is accessible by selective reduction of the less substituted double bond of dienone **4** which in turn is readily prepared by allylic oxidation of diene **5**. Alcohols **6** and **7** would be useful intermediates from which various other C-3 substituted compounds could be prepared by established methods. From an antithetic analysis, the alcohols are obtainable from the $\Delta^{1,10a}$ homoallylic alcohol **8** by selective catalytic reduction. The cis A/B ring juncture is known to be the more thermodynamically favored isomer in decalin systems where the angular substituent is larger than hydrogen.[3] Wenkert and Stevens[4] have shown that catalytic reduction of $\Delta^{1,10a}$ olefins of 4a-methyloctahydrophenanthrenes can lead to predominantly cis compounds. Also, Thompson, McPherson, and Lences[5] have reported stereochemical control in the catalytic reduction of homoallylic alcohols similar to **8** by altering the haptophilicity (electron-donating ability) of the alcohol moiety with various solvents under neutral, acidic, and basic conditions and by transforming the alcohol into the acetate. Thus, by the proper selection of reaction conditions, we can obtain alcohols **6** and **7** stereoselectively from **8**. The transformation of diene **5** into alcohol **8** will be accomplished by regiospecific hydroboration–oxidation[6] of the $\Delta^{3,4}$ double bond. Rabideau and Harvey[7] have obtained diene **5** from phenanthrene by reductive alkylation with lithium in liquid ammonia followed by addition of methyl bromide. The strategy for the preparation of these compounds is illustrated in Scheme I. Diene **5** is a synthon which has the functionality appropriate for use to regio- and stereoselectively introduce substituents at various positions in the tricyclic ring system. It, therefore, represents a key intermediate.

Compounds Substituted at C-2. The reductive alkylation of phenanthrene proceeded smoothly when 5 equiv of lithium were used and the methyl bromide was added rapidly (in large excess), followed by addition of methanol to destroy excess lithium and lithium amide. This provided diene **5** in excellent yield (>95%) containing a trace (up to 3%) of the isomeric conjugated diene. These dienes were readily separated by chromatography on silver nitrate impregnated silica but were normally used as a mixture. Allylic oxidation of diene **5** (or mixture of dienes) using a chromium trioxide–pyridine complex formed in situ in dichloromethane[8] led to the production of the 2-octahydrophenanthrone as the only product. The recovery of product from the tarry reaction mixture was facilitated by dissolution (after washing five times with small volumes of dichloromethane) of the tarry parcipitate with dilute hydrochloric acid and extraction of the aqueous phase with additional dichloromethane. The dienone was conveniently purified by chromatography on silica with chloroform as eluent. Isolated yields of dienone were in excess of 80%.

Initial attempts to selectively reduce the less substituted double bond of the dienone were not successful. However, the procedure of Engel et al.[9] employing freshly prepared[10] homogeneous catalyst tris(triphenylphosphine)rhodium chloride gave essentially pure enone after the uptake of 1 equiv of hydrogen. This enone was selectively reduced to the desired ketone **1** by lithium in liquid ammonia and selectively reduced to desired ketone **2** by catalytic hydrogenation over palladium on carbon.[4] The yield of trans ketone **1** was improved if the initial reduction mixture was oxidized with Jones reagent before purification. The

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(1) Cf. *Terpenoids Steroids*, **6**, 116 (1976), and references therein.
(2) The term cis will be used to designate 10aβ-H and trans to designate 10aα-H. Therefore ketone **1** will be called the *trans* ketone and **2** the cis ketone.
(3) (a) F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958); (b) W. S. Johnson, *Acc. Chem. Res.*, **1**, 1 (1968).
(4) E. Wenkert and T. Stevens, *J. Am. Chem. Soc.*, **78**, 2318, 5627 (1956).
(5) H. W. Thompson, E. McPherson, and B. L. Lences, *J. Org. Chem.*, **41**, 2903 (1976).
(6) H. C. Brown, "Organic Synthesis Via Boranes", Wiley-Interscience, New York, 1975.
(7) P. W. Rabideau and R. G. Harvey, *J. Org. Chem.*, **35**, 25 (1970).
(8) D. S. Fullerton and C. M. Chen, *Synth. Commun.*, **6**, 217 (1976).
(9) C. R. Engel, S. Salvi, and M. N. Chowdury, *Steroids*, **25**, 781 (1975).
(10) A. Birch and K. Walker, *J. Chem. Soc. C*, 1894 (1966).

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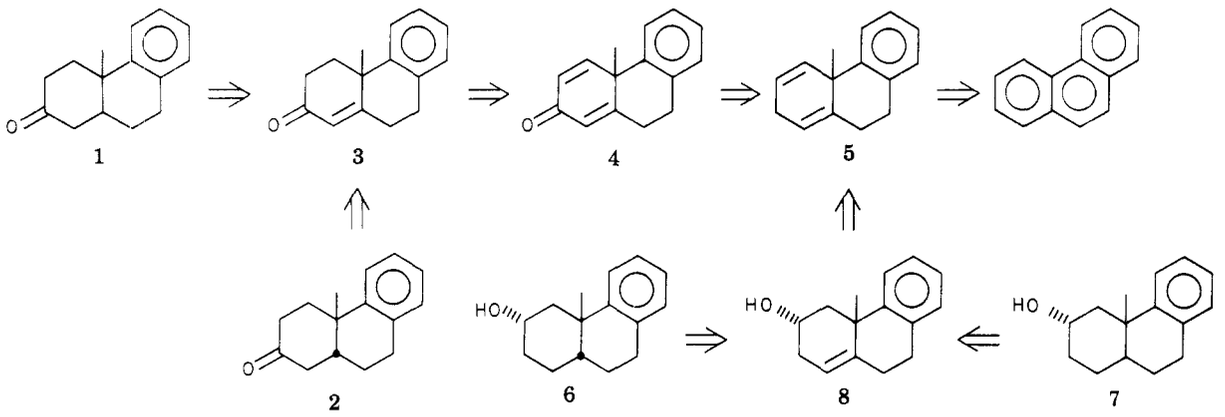
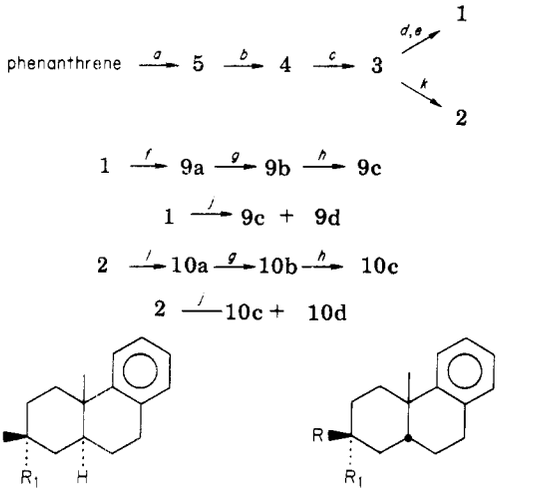
Scheme I



Scheme II



9a, R = OH; R_1 = H
b, R = OTs; R_1 = H
c, R = H; R_1 = $N(CH_3)_2$
d, R = $N(CH_3)_2$; R_1 = H
e, R = R_1 = H

10a, R = H; R_1 = OH
b, R = H; R_1 = OTs
c, R = $N(CH_3)_2$; R_1 = H
d, R = H; R_1 = $N(CH_3)_2$

[a] Li/NH_3; CH_3Br, CH_3OH. [b] $CrO_3 \cdot 2pyr/CH_2Cl_2$. [c] $H_2/(Ph_3P)_3RhCl$. [d] Li/NH_3, *t*-BuOH. [e] CrO_3/H_2SO_4/acetone. [f] $LiAl(O\text{-}t\text{-}Bu)_3H$. [g] TsCl/pyr. [h] $NH(CH_3)_2/Me_2SO$. [j] $NH(CH_3)_2/H_2/Pd/C$. [k] $H_2/Pd/C$/ethanol. [l] $NaAl(OCH_2CH_2OCH_3)_2H_2$/benzene.

lithium in ammonia reduction apparently leads to substantial overreduction.

Treatment of ketone **1** with lithium tri-*tert*-butoxyaluminum hydride, a reagent known to reduce unhindered alicyclic ketones to equatorial alcohols,[11,12] gave alcohol **9a** whose spectral properties supported its assigned structure. The tosylate **9b** was formed by treatment of the alcohol with tosyl chloride in pyridine and then displaced with dimethylamine in Me_2SO to give the axial dimethylamino derivative, 2α-(*N*,*N*-dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (**9c**). Spectral and physical properties were in accord with the assigned structure. The isomeric 2β-(*N*,*N*-dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (**9d**) was readily prepared as the major product from the direct reductive amination of ketone **1** with hydrogen over palladium on carbon in the presence of dimethylamine. The isomeric trans amines were readily separated by column chromatography on neutral alumina. The spectral characteristics and physical properties as well as its formation in a ratio of 5:1 over the minor isomer corraborate the assignment of an equitorial position (2β) to the *N*,*N*-dimethylamino group of the major reductive amination product.

Reduction of ketone **2** with sodium bis(2-methoxyethoxy)aluminum hydride in benzene and recrystallization of the product from petroleum ether gave known[13] alcohol **10a**. Tosylation with tosyl chloride in pyridine yielded tosylate **10b** which was reacted with dimethylamine in Me_2SO at 80 °C in a closed system to yield the dimethylamino derivative 2β-(*N*,*N*-dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10β-octahydrophenanthrene **10c**. Reductive amination of ketone **2** with hydrogen over palladium on carbon in the presence of dimethylamine gave a 3:2 mixture of the C-2-α (10d) and β (10c) isomers. As expected, these were not readily separated by chromatography since in the conformationally flexible cis fused A/B ring juncture both C-2 substituents may assume equatorial orientations by simple ring flip. Spectral properties of the isomers are in accord with this explanation.

Compounds Substituted at C-3. The hydroboration–oxidation of the diene **5** using 9-borobicyclo[3.3.1]nonane or disiamylborane followed by basic hydrogen peroxide led to the regio- and stereoselective production of the 3α-homoallylic alcohol **8**. The regioselectivity can be accounted for by attack of the hindered boranes on the more accessible C-3 carbon of the least hindered $\Delta^{3,4}$ double bond. The stereoselectivity is consistent with the postulation that the α face of the tetrahydrophenanthrene ring system is less sterically hindered than the β face which contains the angular 4a-methyl group (similar to the steroids). During the investigation of the hydroboration of the mixture of dienes derived from phenanthrene reductive alkylation, it was observed that diene **5** reacted much faster than its conjugated isomer. Taking advantage of this difference in reactivities, the conjugated diene could be completely recovered unchanged from the reaction mixtures in which diene **5** was totally converted to alcohol **8**.

Catalytic hydrogenation of **8** produced the cis and trans alcohols **6** and **7**. This reduction was found to be extremely solvent and pH dependent. When alcohol **8** was reduced with platinum oxide in ethanol with a trace of acid present, **6** and **7** were formed in a 95:5 ratio. However, reduction in hexane provided **6** and **7** in a 1:1 ratio, and when the corresponding acetate of **8** was reduced in acetic acid alcohols **6** and **7** were produced in a 25:75 ratio. This result is not consistent with the haptophilicity argument of

(11) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 1431 (1958).
(12) A. W. Burgstahler and I. C. Nordin, *J. Am. Chem. Soc.*, **83**, 198 (1961).
(13) F. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 1248 (1958).

Table I. Azide Displacement

R group	reaction temp, °C	azide (% yield)	olefin
cis-α-OTs (11d)	105	β (51)	12
cis-α-OMs (11e)	105	β (50)	12
cis-β-OTS (11j)	85	α (63)	12
trans-β-OTs (14c)	75	α (66)	15, 16 (2:3)

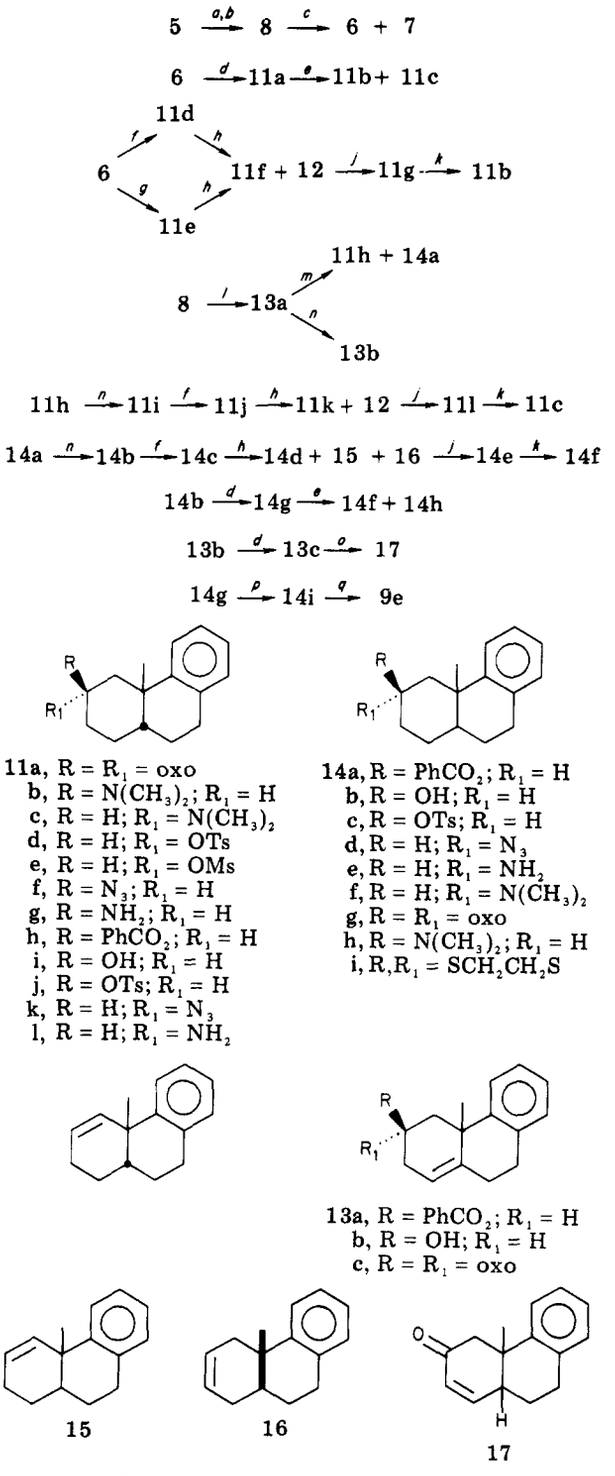
Thompson and co-workers.[5] All attempts to take advantage of this selectivity failed because the trans alcohol **7** could not be separated from the cis alcohol **6** by the preparative chromatography. Thus, only the cis 3α-alcohol **6** could be obtained from catalytic reduction of **8**. Jones oxidation of alcohol **6** to the cis ketone **11a** followed by reductive amination with dimethylamine and sodium cyanohydridoborate as described by Borch[14] produced the desired 3β- and 3α-(*N*,*N*-dimethylamines) **11b** and **11c** in a 75:25 ratio and in moderate yield (75%). The best yields for this reductive amination procedure were obtained when the reaction was run in the presence of 3A molecular sieves. As with alcohols **6** and **7**, all attempts to separate the dimethylamines **11b** and **11c** on a preparative scale by chromatography failed.

Due to our inability to separate **11b** and **11c**, we chose to synthesize each of the cis dimethylamines stereospecifically. This was accomplished for the 3β isomer **11b** by potassium azide displacement of the α-tosylate **11d** or α-mesylate **11e** derived from the α-alcohol **6**. The reaction of an azide with a secondary halide[15] or tosylate[16] has been established to be stereospecific and to involve Walden inversion, thus, only the 3β azide was obtained from the 3α-tosylate. A competing reaction with S_N2 displacement of secondary tosylates is E_2 elimination and olefin **12** was also obtained.

The 3β-azide **11c** was converted to the *N*,*N*-dimethylamine **11b** by reduction with lithium aluminium hydride to the primary amine **11g** followed by the Eschweiler–Clarke method[17] for reductive alkylation with formaldehyde and formic acid in an overall isolated yield of 89% from the azide.

To complete the synthesis of the remaining isomers in series I, we needed the cis 3β-alcohol and a convenient entry into the trans series of compounds. Thus, we speculated the inversion of the 3α-homoallylic alcohol **8** to the 3β-benzoate **13a** followed by catalytic reduction of the 1,10a double bond would produce a mixture of the cis and trans 3β-benzoates. Catalytic reduction of **13a** was anticipated to favor the formation of the trans isomer due to the increased steric bulk of the β face of the olefin. Also, we believed chromatography would allow the separation of **11h** and **14a** because the trans isomer **14a** is rigidly held in the axial orientation while the cis isomer **11h** can become equatorial due to the flexibility of the cis ring juncture. Thus, the synthesis was attempted as shown in Scheme III. The inversion reaction, as described by Bose,[18] proceeded smoothly but only in moderate yield (66%) with the concominant formation of dienes **5** and its conjugated isomer in a 1:1 ratio. Catalytic reduction of **13a** proceeded as expected with a cis/trans ratio of 2:3. Furthermore, the complete separation of **11h** and **14a** was easily accomplished by pressure assisted preparative liquid chromatography.

Scheme III



[a] 9-BBN. [b] H_2O_2/NaOH. [c] H_2/Pd/C/EtOH/H^+. [d] CrO_3/H_2SO_4/acetone. [e] $NH(CH_3)_2/NaBH_3CN$. [f] TsCl/pyr. [g] MsCl/pyr. [h] KN_3/DMF. [j] $LiAlH_4$. [k] CH_2O/HCO_2H. [l] $Ph_3P/PhCO_2H/EtO_2C{-}N{=}NCO_2Et$/THF. [m] H_2/Pd/C/hexane/THF. [n] KOH/EtOH/H_2O. [o] *p*-ToSH/benzene. [p] $HSCH_2CH_2SH/BF_3{\cdot}Et_2O$. [q] Raney Nickel/EtOH.

The cis 3β-benzoate **11h** was transformed into the cis 3α-(*N*,*N*-dimethylamine) **11c** as shown in Scheme III. Hydrolysis of the benzoate **11h** with aqueous potassium hydroxide in ethanol afforded the 3β-alcohol **11i**. Formation of tosylate **11j** followed by potassium azide displacement produced the 3α-azide **11k** and olefin **12**. (See

(14) R. F. Borch, M. D. Berstein, and H. D. Durst, *J. Am. Chem. Soc.*, **93**, 2897 (1971).
(15) Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. Rao, *Nature (London)*, **166**, 178 (1950).
(16) C. W. Shoppee and R. J. Stephenson, *J. Chem. Soc.*, 2230 (1954).
(17) M. L. Moore, *Org. React.*, **5**, 301 (1949).
(18) A. K. Bose, B. Lal, W. A. Hoffman, III, and M. S. Manhas, *Tetrahedron Lett.*, 1619 (1973).

Table I.) Azide **11k** was converted to the 3α-(*N*,*N*-dimethylamine) **11c** as described for azide **11f** in excellent overall yield (87%).

Conversion of the trans 3β-benzoate **14a** into the 3α-(*N*,*N*-dimethylamine) **14f** was accomplished as shown in Scheme III. The sequence is identical with that described for benzoate **11h**. The formation of the trans 3α-azide **14d** occurred in 66% yield with formation of two olefins **15** and **16**. (See Table I.) Again azide **14d** was smoothly converted into the desired 3α-(*N*,*N*-dimethylamine) **14f**.

The results in Table I for the azide displacement of the cis and trans β-tosylates are consistent with attack from the less hindered α face of the octahydrophenanthrene. Therefore, lower reaction temperatures can be employed which reduces the amount of olefin formed. Also, an observation worthy of note, the only olefin obtained from the azide displacement of the cis 3α- and β-tosylates is, surprisingly, the $\Delta^{3,4}$ olefin **12**. However, in the trans 3β-tosylate displacement, both the $\Delta^{3,4}$ and $\Delta^{2,3}$ olefins were obtained in a 2:3 ratio.

The 3β-(*N*,*N*-dimethylamine) **14h** was prepared by Jones oxidation of the trans 3β-alcohol **14b** followed by reductive amination of ketone **14g** with dimethylamine and sodium cyanohydridoborate which led to the formation of the 3α- and 3β-(*N*,*N*-dimethylamines) in 15:85 ratio. The preferential formation of the 3β isomer **14h** is consistent with the results obtained from reductive amination of the cis ketone **11a** in which the 3β isomer **11b** was selectively formed in a 75:25 ratio. In both cases, attack of the cyanohydridoborate on the intermediate *N*,*N*-dimethylimminium ion occurred from the least hindered α face of the octahydrophenanthrene nucleus. However, in contrast to the cis *N*,*N*-dimethylamines, separation of the trans isomers was easily accomplished by column chromatography.

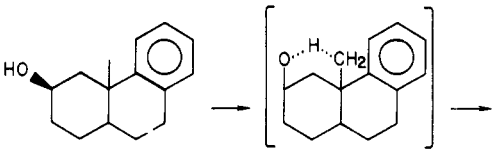
Chemical Verification of Stereochemistry. The intermediacy of ketones **1** and **2** and of the alcohol **10a**, all of well-established structure and stereochemistry, provides the necessary landmarks for establishing the stereochemistry of the compounds prepared in this study which are substituted at C-2 of the 4a-methyloctahydrophenanthrene ring system. However, such was not the case for compounds of the C-3 substituted series.

The key compound in the unambigous assignment of stereochemistry for all the structures of the C-3 series is alcohol **14b**.

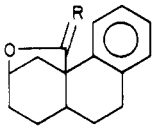
The structure of **14b** was established in the following manner. Oxidation of **14b** produced a ketone **14g** which incorporated four deuteriums without affecting the stereochemistry of the A/B ring juncture or the C-9 benzylic hydrogens. From these results, we could have either a C-2 or C-3 ketone. The C-2 position could be ruled out because ketone **14g** was different from known ketones **1** and **2** obtained from the stereospecific reductions of enone **3**.

Also, oxidation of alcohol **8**, obtained from hydroboration–oxidation of diene **5**, produced an unconjugated enone **13c** which could be isomerized to the corresponding conjugated enone **17**. This conjugated enone was different from enone **3** and contained a mixture of isomers at the A/B ring juncture. Based on this information, we can assign the C-3 position to alcohol **14b**.

The β orientation of the C-3 hydroxyl group was demonstrated by its ability to undergo an intramolecular free-radical hydrogen-transfer reaction similar to the Barton reaction.[19] Detailed examination of a wide range of examples has led to the conclusion that this reaction proceeds in discrete steps, and the hydrogen transfer step is strongly favored by the possibility of a six-membered cyclic transition state.[20] Therefore, when alcohol **14b** was



14b



18a, R = H_2
b, R = O

irratiated with ultraviolet light in the presence of iodine and lead tetraacetate, as described by Akhtar and Barton,[21] cyclic ether **18a** and lactone **18b** were formed in excellent yield (68%) for this type of transformation.

Formation of lactone **18b** is unusual but can be explained by the presence of oxygen in the reaction mixture because the normal method to ensure an oxygen free system (bubbling inert gas through the solvent during the reaction) was not used. In any case, both **18a** and **18b** establish the β configuration and further substantiate the C-3 position of the hydroxyl group in **14b**.

In the previous discussion, we have established that compound **14b** contains a 3β alcohol. The only remaining structural feature still undetermined concerns the nature of the A/B ring juncture. The hydrogen at the 10a position was shown to have the α configuration from analysis of hydrocarbon **9e**, which was obtained from ketone **14g** by Raney nickel reduction of the ethylenethioketal **14i**. The spectral characteristics of **9e** were identical with those reported by Wenkert and co-workers.[22] The stereochemistry of hydrocarbon **9e** was established by Barnes and Beachem[23] using the method of Backman and Kushner.[24] From these results, we can completely describe compound **14b** as: 4a-methyl-1,2,3,4,4a,9,10,10aα-octahydro-3β-phenanthrol.

With the stereochemistry of compound **14b** established, we can assign the configuration of 3β-OH, 10aβ-H to alcohol **11i** because both alcohols were derived from the same olefin **13a**.

The 3α stereochemistry of the homoallylic alcohol **8** was established from the Bose reaction product **13a**. This reaction with allylic alcohols has been shown to be stereospecific and to proceed with inversion of configuration.[25] In our case, the inversion was confirmed by hydrolysis of benzoate **13a** producing the 3β homoallylic alcohol **13b** which was different from alcohol **8**.

The stereochemistry of alcohol **6** at the C-3 position must be α because it was obtained from the 3α-alcohol **8** by catalytic reduction. The configuration at the A/B ring juncture was shown to be 10αβ by Jones oxidation to a ketone which was identical with the 10αβ ketone **11a** obtained from Jones oxidation of alcohol **11i**.

(19) D. H. Barton, J. Beaton, L. Geller, and M. Pechet, *J. Am. Chem. Soc.*, **83**, 4076 (1961).

(20) W. Carruthers, "Some Modern Methods of Organic Synthesis", Cambridge University Press, New York, 1971, p 183.

(21) A. Akhtar and D. H. Barton, *J. Am. Chem. Soc.*, **86**, 265 (1964).

(22) E. Wenkert, A. Afonso, P. Beak, R. Carney, P. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965).

(23) R. A. Barnes and M. T. Beachem, *J. Am. Chem. Soc.*, **77**, 5388 (1955).

(24) W. E. Backmann and S. Kushner, *J. Am. Chem. Soc.*, **65**, 1963 (1943).

(25) G. Grykiewicz and H. Burzniska, *Tetrahedron*, **32**, 2109 (1976).

Having established the stereochemistry of alcohols **6**, **11i**, and **14b**, we can assign the stereochemistry of the corresponding azides **11f**, **11k**, and **14d** because the azide displacement of secondary tosylates, as discussed previously, has been established to be stereospecific and to involve Walden inversion. Therefore, the azides obtained possess the opposite C-3 configuration of the precursor alcohols (i.e., 3α-OH **6** → cis 3β-N_3 **11f**). This allows the complete assignment of stereochemistry of the corresponding *N,N*-dimethylamines because the reactions involved in the transformation of the azides into the dimethylamines (lithium aluminium hydride reduction followed by reductive amination) have been shown to retain the stereochemistry of the starting azides.[26] Thus, the structures of compounds **11b**, **11c**, and **14f** are as shown.

The stereochemistry of the remaining 10aβ-(dimethylamine) **14h** was established by comparison with **14f**. A 15:85 mixture of dimethylamines was obtained from reductive amination of the 10aα ketone **14g**. Unlike the 10aβ-(dimethylamines), the 10aα isomers were easily separated by chromatography. The minor isomer was identical with **14f** obtained from azide **14d**. Therefore, the major isomer must be **14h**: 3β-(*N,N*-dimethylamino)-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene.

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 spectrophotometer using a KBr wafer unless stated otherwise. Proton magnetic resonance spectra were obtained with a Varian Associates EM-360 spectrometer with tetramethylsilane as internal standard and deuteriochloroform as solvent. In ^1H NMR descriptions, s = singlet, d = doublet, t = triplet, m = multiplet, and dd = doublet of doublets. Mass spectra were recorded using a Varian Associates CH-5 spectrometer; ionization was by electron impact. Microanalyses were performed on a Hewlett-Packard 185 B CHN analyzer at the University of Kansas. Gas Chromatographic analyses were conducted using a Varian Associates Model 3700 analytical gas chromatograph equipped with a flame-ionization detector and a 3 m × 2 mm 6% SE-30 column on Chromosorb W (100 mesh). Helium was used as carrier gas, and the flow rate was ca. 35 mL/min. Silylation for gas chromatographic purposes was routinely performed on 10 mg of substrate with Regisil (bis(trimethylsilyl)trifluoroacetamide) in pyridine (50 μL) heated to 50 °C for 5 min. All ratios of isomeric mixtures were determined by GLC and ^1H NMR analysis.

Liquid chromatography was performed with columns of length to width ratios 75:1 using Brinkman silica gel 60 (70–325 mesh) and solvent system A 99.5 EtAc/0.5 MeOH/NH_4OH or as indicated. Preparative and thin-layer chromatography were performed on Brinkman precoated plates. Preparative scale pressure assisted liquid chromatography using Merck silica gel 60 (230–400 mesh) was performed at ca. 70 psi with 10 cm × 1.5 cm glass columns and a solvent flow rate of ca. 20 mL/min. Solvents for chromatography were distilled before use.

Tetrahydrofuran was distilled from $LiALH_4$ just prior to use. All other solvents were purified according to literature procedures and stored under dry nitrogen over 4 Å molecular sieves. All reactions using dry solvents were run under a positive pressure nitrogen atmosphere. Usual workup of reaction products involved extraction with a solvent, washing with saturated NaCl, drying with K_2CO_3, and evaporation in vacuo (rotating evaporator).

4a-Methyl-2,4a,9,10-tetrahydrophenanthrene (5). A modification of Rabideau and Harvey's[7] procedure was used. Ammonia (2 L) was condensed into a flame-dried, three-necked, round-bottom flask (4 L) equipped with a glass paddle mechanical stirrer, dry ice condenser, and pressure equalizing addition funnel. Phenanthrene (75.0 g, 0.42 mol) in dry THF (750 mL) was added to refluxing ammonia (−34 °C) followed by small pieces (0.25 cm) of lithium wire (15.5 g, 2.24 mol) in a stream of nitrogen. The resultant blue-green solution gradually turned dark red while it was being stirred for 30 min at −34 °C. Methyl bromide (129.8 g, 1.38 mol) in THF (50 mL) cooled to −78 °C was rapidly added to this red solution. **Caution**: Reaction is extremely exothermic. The clear solution was stirred for 5 min and then MeOH (250 mL) was added to consume excess lithium and to neutralize any lithium amide present. The volatiles were evaporated under reduced pressure, and the residue was taken up in an ether/water (5:1) mixture (500 mL). The aqueous layer was separated, saturated with NaCl, and extracted with ether (3 × 100 mL) affording a yellow oil (78.9 g). Vacuum distillation (102–104 °C (2 mm)) provided 77.0 g (94%) of a mixture of **5** and 4a-methyl-4,4a,-9,10-tetrahydrophenanthrene in a 97:3 ratio. A portion of this diene mixture (10.0 g) was chromatographed on 10% silver nitrate impregnated silica (600 g) with hexane/ether (99:1) yielding **5** (8.1 g) and 4a-methyl-4,4a,9,10-tetrahydrophenanthrene (0.15 g). The physical and spectral properties of both compounds were identical with those previously reported.[7]

4a-Methyl-9,10-dihydro-2(4a*H*)-phenanthrone (4). Dienone **4** was prepared according to the method of Fullerton and Chen.[8] To an ice-bath cooled, rapidly mechanically stirred solution of anhydrous pyridine (12.8 mL, 12.5 g, 150 mmol) in dry CH_2Cl_2 was added chromium trioxide (7.5 g, 75 mmol). The deep burgundy solution was stirred for 5 min then allowed to warm to 25 °C. After being stirred for 10 min, a solution of diene **5** (0.98 g, 5.0 mmol) in CH_2Cl_2 (10 mL) was added in one portion. A tarry precipitate immediately began forming on the sides and bottom of the flask. After 5 h of stirring at 25 °C, TLC (hexane) indicated very little starting material remained. Thus, the CH_2Cl_2 was decanted and the tarry precipitate was washed with CH_2Cl_2 (5 × 25 mL). The extracts were combined and concentrated in vacuo. The oily residue was taken up in ether, filtered, and washed with 15% HCl (2 × 50 mL) to yield an orange oil (0.90 g). Chromatography on silica (25 g) with $CHCl_3$ yielded 0.10 g of dienes and 0.77 g (82% based on recovered **5**) of dienone **4**: mp 79.0–79.5 °C (pentane/ether); IR 1665, 1630, 1605, 1490, 1455, 1445 cm^{-1}; NMR δ 7.50–6.90 (m, 5, 4 aromatic H and C-4 vinyl H), 6.32–6.06 (m, 2, C-3 and C-1 vinyl H), 3.20–2.50 (m, 4, benzylic and allylic H), 1.50 (s, 3, CH_3); MS, *m/e* 210 (M^+), 195, 182, 167 (base), 165.

Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.75; H, 6.85.

4a-Methyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrone (3). Enone **3** was prepared according to the procedure of Engel and co-workers.[9] To dienone **4** (210 mg, 1.0 mmol) in dry benzene (25 mL) was added tris(triphenylphosphine)rhodium chloride (160 mg, prepared according to the method of Birch[10]), and the solution was hydrogenated for 2.5 h at 28 psi and 25 °C with a Parr Series hydrogenation apparatus. The clear red solution was concentrated in vacuo and then absorbed onto silica (10 g). Elution with $CHCl_3$ gave 180.2 mg (85%), mp 89–90 °C [lit.[13] mp 90 °C].

4a-Methyl-3,4,4a,9,10,10aα-hexahydro-2(1*H*)-phenanthrone (1). The method of Wenkert and Stevens[4] was used. To a solution of lithium (2.8 g, 0.405 g-atom) in distilled NH_3 (500 mL) was added compound **3** (5 g, 0.0236 m) in Et_2O (100 mL). After 3 h NH_4Cl (25 g) was added and the NH_3 was allowed to evaporate. Water (100 mL) was added, and the solution was extracted four times with Et_2O (50 mL). The ethereal extracts were washed with 3 N HCl and H_2O, dried ($MgSO_4$), and concentrated to give 4.8 g of a brown solid: IR (KBr) 3300–3600 (OH), 1700 (C=O), and 1660 cm^{-1} (conjugated C=O). Jones oxidation[27] followed by column chromatography on neutral alumina (activity II) using 5% Et_2O–petroleum ether as the eluent gave 3.4 g (69%) of compound **1**: mp 105–106 °C (lit.[4] mp 106 °C); IR (KBr) 1709 cm^{-1} (C=O); NMR δ 1.32 (s, 3, CH_3), 2.8–3.0 (m, 2, benzylic H), and 7.1–7.4 (m, 4, aromatic).

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-2β-phenanthrol (9a). Ketone **1** (0.130 g, 0.613 mmol) in THF (50 mL) was reduced with $LiAl(O\text{-}t\text{-}Bu)_3H$ (0.254 g, 1.00 mmol) at 0 °C for 1 h and then at 25 °C for 12 h. The solution was acidified with 3 N HCl (50 mL) and extracted four times with Et_2O (25 mL). The ethereal

(26) A. K. Bose, J. F. Kistner, and L. Farber, *J. Org. Chem.*, **27**, 2925 (1962).

(27) C. Djerassi, R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

extracts were combined, washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a colorless oil. The oil, when chromatographed on a column of neutral alumina (activity II) using 50% Et_2O–petroleum ether as the eluent, gave 0.035 g of compound **9a**: NMR 3.5 (m, 1, half-band width 21 Hz, axial 2α-C**H**–OH).

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-2β-phenanthrol Tosylate (9b). To a solution of compound **9a** (0.035 g, 0.162 mmol) in pyridine (5 mL) at 0 °C was added TsCl (0.0665 g, 0.349 mmol). The flask was stoppered and placed in the refrigerator for 12 h. The solution was poured into ice water (50 mL) and extracted four times with Et_2O (50 mL). The ethereal extracts were combined, washed with 3 N HCL and H_2O, dried (Na_2SO_4), and concentrated to give 0.083 g of an oil: NMR δ 4.5 (m, 1, half-band width 21 Hz, axial 2α-C**H**OTs).

2α-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (9d). A solution of compound **9b** (0.083 g, 0.22 mmol), dimethylamine (20 mL), and Me_2SO (15 mL) was placed in a reaction bomb and heated at 70 °C for 3 days. The solution was poured into H_2O (50 mL) and extracted four times with Et_2O (50 mL). The ethereal extracts were combined, washed with saturated NaCl solution, dried (Na_2SO_4), and concentrated in vacuo to remove dimethylamine and solvents to give 0.0882 g of compound **9d**: NMR (CCl_4) δ 1.08 (s, 3, CH_3), 2.16 (s, 6, N**Me**$_2$).

The methiodide was prepared in C_6H_6 and recrystallized from MeOH–Et_2O, mp 219.5–221 °C.

Anal. Calcd for $C_{16}H_{28}IN$: C, 56.10; H, 7.32; N, 3.64. Found: C, 56.33; H, 7.42; N, 3.86.

2-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (9c and 9d). A solution of compound **1** (0.9 g, 4.2 mmol), 25% aqueous dimethylamine (50 mL), and EtOH (100 mL) was hydrogenated in the presence of 10% Pd/C (0.578 g) for 24 h at 32 psi in a Parr apparatus. The catalyst was removed by filtration, and the filtrate was concentrated to ca. 50 mL and extracted four times with Et_2O (25 mL). The ethereal extracts were combined, washed with saturated NaCl solution, dried (Na_2SO_4), and concentrated in vacuo to remove the excess dimethylamine and Et_2O, to give an oil. The oil was chromatographed on a column of neutral alumina (activity II). Five percent Et_2O–petroleum ether as the eluent gave 0.1515 g (14.8%) of compound **9d** and 40% Et_2O–petroleum ether as the eluent gave 0.7627 g (74.5%) of compound **9c**: NMR (CCl_4) δ 1.06 (s, 3, CH_3), 2.25 (s, 6, N**Me**$_2$).

The methiodide was prepared in C_6H_6 and recrystallized from MeOH–Et_2O, mp 195–197 °C.

Anal. Calcd for $C_{18}H_{28}IN$: C, 56.10; H, 7.32; N, 3.64. Found: C, 55.94; H, 7.53; N, 3.88.

4a-Methyl-3,4,4a,9,10,10aβ-hexahydro-2(1*H*)-phenanthrone (2). The procedure of Wenkert and Stevens[4] was followed. A solution of compound **3** (3 g, 14.0 mmol) in EtOH (100 mL) was hydrogenated in the presence of 5% Pd/C (1 g) for 5 h at atmospheric pressure in a microhydrogenator apparatus. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo. The residue was taken up in Et_2O, washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a colorless liquid. The liquid, when chromatographed on a column of neutral alumina (activity II) using C_6H_6–petroleum ether (3:1) as the eluent, gave 2.56 g (85%) of compound **2** as an oil: IR (liquid film) 1720 cm^{-1} (C=O); NMR δ 1.40 (s, 3, C**H**$_3$), 2.8–3.0 (m, 2, benzylic H), and 7.1–7.4 (m, 4, aromatic).

The semicarbazide was prepared in EtOH–H_2O and recrystallized from EtOH–H_2O, mp 194–196 °C (lit.[4] mp 195–197 °C).

Anal. Calcd for $C_{16}H_{21}N_3O$: C, 70.81; H, 7.80; N, 15.49. Found: C, 70.79; H, 8.03; N, 15.10.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-2α-phenanthrol (10a). A solution of 70% red-Al [$NaAl(OCH_2–CH_2–OCH_3)_2H_2$] (0.28 g, 1.7 mL, 1.4 mmol, Aldrich Chem. Co.), ketone **2** (1.93 g, 9.05 mmol), and benzene (25 mL) was refluxed for 2 h and cooled, 1 N NaOH (25 mL) was added, and the solution was extracted four times with Et_2O (100 mL). The ethereal extracts were combined, washed (H_2O), dried ($MgSO_4$), and concentrated to give a white solid. Recrystallization of the solid in petroleum–ether gave 0.28 g of compound **10a**: mp 76.5–77.5 °C (lit.[13] mp 75–77 °C); NMR (CCl_4) δ 1.13 (s, 3, C**H**$_3$), 3.5 (m, 1, half-band width 22 Hz, axial 2β-C**H**OH).

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-2α-phenanthrol Tosylate (10b). To a solution of alcohol **10a** (0.203 g, 0.95 mmol) in pyridine (25 mL) was added TsCl (0.38 g, 2.0 mmol). The flask was stoppered and placed in the refrigerator for 48 h. The solution was poured into ice water (100 mL) and extracted four times with Et_2O (50 mL). The combined ethereal extracts were washed with 3 N HCl and H_2O, dried (Na_2SO_4), concentrated, and crystallized from petroleum ether to give 0.256 g (74%) of tosylate **10b**: mp 90–91 °C: NMR (CCl_4) δ 1.10 (s, 3, CH_3), 4.5 (m, 1, half-band width 22 Hz, axial 2β-C**H**OTs).

2β-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (10c). A solution of tosylate **10b** (0.137 g, 0.87 mmol), dimethylamine (10 mL), and Me_2SO (10 mL) was placed in a reaction bomb and heated at 80 °C for 8 days. The solution was poured into H_2O (300 mL) and extracted four times with Et_2O (50 mL). The ethereal extracts were combined, washed with saturated NaCl solution, dried (Na_2SO_4), and concentrated in vacuo to remove excess dimethylamine and Et_2O to give an oil. The oil was chromatographed on a preparative thin-layer plate (Brinkman, 2 mm, 20 × 20 cm) of alumina F and developed with Et_2O–petroleum ether (1:1) to give 0.084 g of amine **10c** as an oil: NMR (CCl_4) δ 1.31 (s, 3, CH_3), 2.20 (s, 6, NMe_2). A sample was microdistilled for analysis.

Anal. Calcd for $C_{15}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.57; H, 10.55; N, 5.85.

2-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (10c and 10d). A solution of ketone **2** (1.74 g, 8.14 mmol), 25% aqueous dimethylamine (100 mL), and EtOH (100 mL) was hydrogenated in the presence of 5% Pd/C (1 g) for 16 h at 27 psi in a Parr apparatus. The catalysts was removed by filtration, and the filtrate was concentrated to ca. 50 mL and extracted four times with Et_2O (50 mL). The ethereal extracts were combined, washed with saturated NaCl solution, dried (Na_2SO_4), and concentrated in vacuo to give an oil. The oil, when chromatographed on a column of neutral alumina (activity II) using Et_2O–petroleum ether as the eluent, gave 1.9 g of a mixture of **10c** and **10d** as an oil: NMR (CCl_4) δ 1.15 (s, CH_3), 1.31 (s, CH_3), 2.08 (s, N**Me**$_2$), 2.20 (s, N**Me**$_2$). Numerous attempts of chromatographic separation were unsuccessful.

4a-Methyl-2,3,4,4a,9,10-hexahydro-3α-phenanthrol (8). Method A. To diene **5** (4.1 g, 20.9 mmol) in dry THF (50 mL) was added 0.5 M 9-bicyclo[3.3.1]borononane (45.6 mL, 2.55 g, 20.9 mmol). The mixture was stirred at 25 °C until the reaction was complete (36-48 h) as evidenced by analysis of 1-mL aliquots (GLC) withdrawn periodically and oxidized as described below. H. C. Brown's oxidative procedure was followed.[6] To the cooled mixture (0 °C) was concurrently added dropwise 3 N NaOH (20 mL) and 30% H_2O_2 (20 mL) while maintaining the temperature below 40 °C. After the addition was complete, the mixture was stirred at 40 °C for 2 h, then the aqueous layer was separated, saturated with NaCl, and extracted with $CHCl_3$ (3 × 50 mL) to yield an oil (9.0 g) containing **8** and 1,5-dihydroxycyclooctane. Chromatography (300 g) with $CHCl_3$ gave a mixture (4.0 g) which solidified on standing. Recrystallization (EtOH/H_2O) yielded 3.5 g (78%) of **8**, mp 107–108.5 °C.

Method B. To diene **5** (5.0 g, 25.5 mmol) in dry THF (50 mL) was added 0.33 N disiamylborane in THF (27 mL) freshly prepared according to H. C. Brown's procedure.[6] Stirring at 25 °C for 1 h then at 35 °C for 6 h resulted in complete consumption of diene **5** as evidenced by GLC of a worked up 1-mL aliquot. Workup was identical with method A, except the oil obtained was distilled (110–120 °C (0.05 mm)) yielding 4.5 g of **8**. Recrystallization (EtOH/H_2O) afforded 4.0 g (73%) of **8**: mp 107–108.5 °C; IR 3330, 3090, 3040, 1030 cm^{-1}; NMR δ 7.38–6.98 (m, 4, aromatic H), 5.38 (m, 1, $W_{1/2}$ = 9.0 Hz vinyl H), 4.20 (m, 1, $W_{1/2}$ = 21.5 Hz, C**H**OH), 3.02–2.02 (m, 6, benzylic and allylic H), 1.80 (m, 2, H-4), 1.61 (broad s, 1, O**H**), 1.42 (s, 3, CH_3); MS, *m/e* 214 (M^+), 199 (base), 196.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.09; H, 8.47. Found: C, 84.19; H, 8.42.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-3α-phenanthrol (6). A solution of **8** (1.0 g, 4.7 mmol) in 95% EtOH (10 mL) and 10% HCl (0.5 mL) was added to prereduced PtO_2 (50 mg) in 95% EtOH (20 mL). The mixture was hydrogenated at 25 °C in a Parr Series 4536 low-pressure hydrogenation apparatus at 28 psi for 5 h. After removal of the catalyst by filtration, the solution was

neutralized with solid $NaHCO_3$ and evaporated to yield a clear oil (1.06 g). Analysis of the silylated alcohols indicated the **10aα** and **10aβ** isomers were present in a 5:95 ratio (GLC). Vacuum distillation (135–137 °C (0.5 mm)) yielded 0.93 g (91%) of **6** as a colorless oil: IR (film) 3360, 1028 cm^{-1}; NMR δ 7.30–6.80 (m, 4, aromatic H), 3.72 (m, 1, $W_{1/2}$ = 24 Hz, CHOH), 2.94–2.42 (m, 2, benzylic HO), 1.30 (s, 3, CH_3); MS, *m/e* 216 (M^+), 198, 183 (base), 141.

Anal Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.03; H, 9.49.

4a-Methyl-1,4,4a,9,10,10aβ-hexahydro-3(2*H*)-phenanthrone (11a). Jones reagent[28] (3.94 mL) was slowly added to a cooled solution (0 °C) of **6** (3.42 g, 15.47 mmol) in acetone (30 mL). The mixture was stirred at 0 °C for 10 min then at 25 °C for 30 min. Excess oxidant was consumed with isopropyl alcohol (1 mL), and the solution was neutralized with solid $NaHCO_3$. The acetone was decanted, and the chromium salts were washed with ether (3 × 15 mL). The organic phases were combined to afford a pale yellow oil (3.01 g). Vacuum distillation (125–130 °C (0.05 mm)) yielded 2.87 g (85%) of **11a**: IR (film) 1715 cm^{-1}; NMR δ 7.22–6.83 (m, 4, aromatic H), 3.00–2.70 (m, 2, benzylic H), 2.74 (AB quartet, 1, J_{BA} = 11.0 Hz, H-4), 2.31 (AB quartet, 1, J_{AB} = 11.0 Hz, H-4), 1.30 (s, 3, CH_3); MS, *m/e* 214 (M^+), 199 (base).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.79; H, 8.39.

3-(*N,N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene. R. F. Borch's reductive amination procedure was followed.[14] To a solution of dimethylamine (661.5 mg, 14.70 mmol) in CH_3OH (25 mL) was added 5 N HCl (0.98 mL, 4.90 mmol), followed by ketone **11a** (525 mg, 2.45 mmol) and $NaBH_3CN$ (620 mg, 9.8 mmol). The resulting solution was allowed to stand over 3 Å Linde molecular sieves for 72 h at 25 °C. Concentrated HCl was added until pH <2, and the CH_3OH was removed in vacuo. The residue was taken up in water (5 mL) and extracted with ether (3 × 20 mL). The aqueous solution was brought to pH >10 with solid KOH, saturated with NaCl, and extracted with $CHCl_3$ (5 × 20 mL) to afford 507 mg (85%) of a colorless oil containing 3β-(*N,N*-dimethylamino)-1,2,3,4,4a,9,-10,10a-octahydrophenanthrene (**11b**) and 3α-(*N,N*-dimethylamino)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**11c**) in a 3:1 ratio.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-3α-phenanthrol Tosylate (11d) was prepared as described by Schleyer.[29] To alcohol **6** (0.67 g, 3.1 mmol) in anhydrous pyridine (5 mL) cooled to 0 °C was added *p*-toluenesulfonyl chloride (1.18 g, 6.20 mmol). After solution was complete, the mixture was stored in the refrigerator (−5.0 °C) for 24 h. The mixture was allowed to warm to 25 °C while being stirred then poured onto ice (10 g) and stirred for 30 min. The resulting oily mixture was extracted with ether (5 × 10 mL). The ethereal extracts were combined and washed twice with cold aqueous HCl (1:1) then with water (2 × 10 mL), affording 1.1 g of **11d** as a clear oil. Crystallization from hexane provided 0.99 g (86%) of **11d**: mp 86–87 °C; IR 1170, 1185 cm^{-1}; NMR δ 7.80–7.60 (m, 2, tosylate ortho H), 7.40–6.90 (m, 6, aromatic H), 4.70 (m, 1, $W_{1/2}$ = 20 Hz, CHOTs), 2.92–2.60 (m, 2, benzylic H), 2.44 (s, 3, tosylate CH_3), 1.29 (s, 3, CH_3); MS, *m/e* 370 (M^+), 198, 183 (base).

Anal. Calcd for $C_{22}H_{26}SO_3$: C, 71.32; H, 7.07. Found: C, 71.10; H, 7.30.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-3α-penanthrol mesylate (11e) was prepared as described for tosylate **11d**. Alcohol **6** (0.60 g, 2.77 mmol) yield 0.88 g of crude **11e**. Crystallization from ether/hexane provided 0.78 g (95%) of **11e**: mp 77–79 °C; IR 1185, 1165 cm^{-1}; NMR δ 7.28–6.80 (m, 4, aromatic H), 4.80 (m, 1, $W_{1/2}$ = 18.0 Hz, CHOMs), 2.87 (s, 3, mesylate CH_3), 1.38 (s, 3, CH_3); MS, *m/e* 294 (M^+) 198, 183 (base).

Anal. Calcd for $C_{16}H_{22}SO_3$: C, 65.28; H, 7.53. Found: C, 64.99; H, 7.60.

3β-Azido-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (11f). A modification of the procedure of A. K. Bose, J. F. Kistner, and L. Barber[30] was used. Tosylate **11d** (240 mg, 0.65 mmol) was added to a heated solution (105 °C) of potassium azide (260 mg, 3.25 mmol) in DMF (75 mL) containing water (1.5 mL) to increase the solubility of the azide. The mixture was heated at 105 °C until no tosylate remained (4–5 h), then the solvent was removed in vacuo and the residue taken up in ether, filtered, and concentrated yielding 0.19 g of a clear oil. Chromatography on silica (5.0 g) by gradient elution (1.0 L) from hexane to hexane/CH_2Cl_2 (3:1) yielded 45.0 mg of olefin (**12**) and 81.2 mg (51%) of **11f** as a clear oil: IR (film) 2090 cm^{-1}; NMR δ 7.29–6.83 (m, 4, aromatic H), 1.20 (s, 3, CH_3); MS, *m/e* 241 (M^+), 198 (base). Olefin **12**: IR (film) 3080, 3040 cm^{-1}; NMR δ 7.32–6.85 (m, 4, aromatic H), 5.93–5.31 (m, 2, vinyl H), 2.98–2.58 (m, 2, benzylic H), 1.21 (s, 3, CH_3); MS, *m/e* 198 (M^+).

3β-Amino-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (11g). Azide **11f** (415 mg, 162 mmol) in dry ether (5 mL) was added with stirring to a solution of $LiAlH_4$ (100 mg, 2.64 mmol) in dry ether (25 mL) cooled to −78 °C with a dry-ice/acetone bath. The mixture was stirred for 2 h then allowed to warm to 25 °C. After 1 h at 25 °C, the reaction was worked up as described by Micovic and Mihailovic.[31] The solution was successively treated with water (0.1 mL), 15% NaOH (0.1 mL), and again with water (0.3 mL). The resulting granular precipitate was filtered and washed with ether. The ethereal solutions were combined to yield 365.0 mg (98%) of **11g** as a colorless oil: IR (film) 3380, 3300 cm^{-1}; NMR δ 7.33–6.85 (m, 4, aromatic H), 1.22 (s, 2, NH_2), 1.18 (s, 3, CH_3); MS, *m/e* 215 (M^+), 200, 83, 56 (base).

The picrate salt was prepared for analysis: yellow needles; mp 223–224 °C dec.

Anal. Calcd for $C_{21}H_{24}N_4O_7$: C, 56.75; H, 5.44; N, 12.61. Found: C, 56.79; H, 5.50; N, 12.41.

3β-(*N,N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (11b). To a solution of crude amine **11g** in 91% formic acid (5.0 mL) was added 37% formaldehyde in water (2.0 mL). The mixture was gently refluxed until TLC (system A) indicated the reaction was complete (8 h). The mixture was concentrated in vacuo and the residue was taken up on 10% HCl (5 mL) and concentrated again. This process was repeated until no formaldehyde could be detected. The residue was again taken up in 10% HCl (10 mL), washed with ether (3 × 10 mL), made basic (pH >10) with solid KOH, saturated with NaCl, and extracted with $CHCl_3$ (5 × 10 mL) providing 182.8 mg (99%) of **11b** as a colorless oil. Molecular distillation (105 °C (0.01 mm)) yielded 168.5 mg (91%) of **11b**: n_D 1.5434; IR (film) 2815, 2790, 1445 cm^{-1}; NMR δ 7.32–6.82 (m, 4, aromatic H), 2.20 (s, 6, N-$(CH_3)_2$), 1.18 (s, 3, CH_3); MS, *m/e* 243 (M^+), 228, 84 (base).

The picrate salt was prepared for analysis: yellow needles (H_2O); mp 160.0–161.0 °C.

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.86. Found: C, 58.30; H, 5.91; N, 11.94.

4a-Methyl-2,3,4,4a,9,10-hexahydro-3β-phenanthrol Benzoate (13a). The benzoate was prepared by G. Grynkiewicz and H. Burzynska's modification[25] of the Bose et al.[18] procedure. Alcohol **8** (1.0 g, 4.66 mmol), triphenylphosphine (2.45 g, 9.33 mmol), and benzoic acid (1.14 g, 9.33 mmol) were dissolved in dry THF (100 mL). A solution of diethyl azodicarboxylate (9.33 mmol) in THF was added dropwise with stirring at room temperature. After 5 h, the solvent was removed in vacuo and the residue was taken up in ether, filtered, and concentrated in vacuo. Chromatography on silica (100 g) by gradient elution (2.5 L) from hexane to $CHCl_3$ yielded 0.4 g of a 1:1 mixture of dienes and 0.80 g (67%) of **13a**: mp 86.5–88 °C (MeOH/H_2O); IR 1718, 1275 cm^{-1}; NMR δ 8.14–7.88 (m, 2, benzoate ortho H), 7.56–6.88 (m, 7, aromatic H), 5.50–5.15 (m, 2, vinyl H and CHOBz), 1.51 (s, 3, CH_3); MS, *m/e* 196 (M^+ − benzoate), 181 (base).

Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 83.22; H, 6.99.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-3β-phenanthrol Benzoate (11h) and 4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-3β-phenanthrol Benzoate (14a). A solution of benzoate **13a** (1.0 g, 3.87 mmol) in 5 mL of hexane/THF (9:1) was added to prereduced 5% Pd/C (50 mg) in hexane/THF (9:1) 30 mL)

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containing trifluoroacetic acid (0.5 mL) and hydrogenated at atmospheric pressure and 25 °C until 1.0 equiv of hydrogen had been consumed (ca. 24 h). After removal of the catalyst by filtration, the solution was washed with saturated $NaHCO_3$, dried, and evaporated to afford 1.08 g of a mixture of benzoates. Pressure assisted liquid chromatography with hexane/CH_2Cl_2 (4:1) as eluent (1.0 L) provided 0.38 g of **11b** and 0.51 g of **14a**.

Benzoate **11h**: mp 74.5–75.5 °C (hexane/ether); IR 1715 1270 cm^{-1}; NMR δ 8.05–7.80 (m, 2, benzoate ortho H), 7.47–6.80 (m, 7, aromatic H), 4.65 (m, 1, $W_{1/2}$ = 22.0 Hz CHOBz), 1.22 (s, 3, CH_3); MS, m/e 198 (M^+ – benzoate), 183 (base).

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.59; H, 7.70.

Benzoate **14a**: mp 75.0–76.5 °C (hexane/ether); IR 1718, 1285 cm^{-1}; NMR δ 8.09–7.83 (m, 2, benzoate ortho H), 7.49–6.82 (m, 7, aromatic H), 5.40 (m, 1, $W_{1/2}$ = 8.0 Hz, CHOBz), 3.02–2.70 (m, 2, benzylic H), 1.29 (s, 3, CH_3); MS, m/e 198 (M^+ – benzoate), 183 (base).

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.73; H, 7.65.

4a-Methyl-2,3,4,4a,9,10-hexahydro-3β-phenanthrol (13b). A solution of benzoate **13a** (115.7 mg, 0.448 mmol) in 25 mL of EtOH/water (9:1) and KOH (0.56 g, 10.0 mmol) was heated (50 °C) with stirring until TLC with hexane/CH_2Cl_2 (1:1) indicated complete conversion (ca. 3 h). The solvent was removed in vacuo, and the residue was dissolved in 10 mL of $CHCl_3/H_2O$ (3:1) saturated with NaCl and extracted with $CHCl_3$ (3 × 10 mL) affording 85.0 mg (89%) of a yellow oil; molecular distillation (110 °C (0.03 mm)) provided 74.3 mg of **13b** as a colorless oil: IR (film) 3370, 3110, 3085, 1040; NMR δ 7.30–6.84 (m, 4, aromatic), 5.33 (m, 1, $W_{1/2}$ = 9.0 Hz, vinyl H), 3.88 (m, 1, $W_{1/2}$ = 20.0 Hz, CHOH), 3.00–2.68 (m, 2, benzylic H), 2.68–1.80 (m, 6, 4 allylic H and 2 H-4), 1.57 (s, 1, OH), 1.42 (s, 3, CH_3); MS, m/e 214 (M^+), 199 (base), 196.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.06; H, 8.47. Found: C, 83.93; H, 8.54.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-3β-phenanthrol (11i). Benzoate **11h** (0.64 g, 2.0 mmol) was hydrolyzed with KOH as described for benzoate (**13a**) yielding 0.41 g (95%) of crystalline alcohol (**11i**): mp 96.5–97.5 °C (hexane); IR 3290, 1020 cm^{-1}; NMR δ 7.30–6.80 (m, 4, aromatic H), 3.32 (m, 1, $W_{1/2}$ = 18.0 Hz, CHOH), 1.88 (s, 1, OH), 1.18 (s, 3, CH_3); MS, m/e 216 (M^+), 199, 198, 183 (base).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.20; H, 9.32. Found: C, 83.09; H, 9.50.

4a-Methyl-1,2,3,4,4a,9,10,10aβ-octahydro-3β-phenanthrol tosylate (11j) was prepared as described for the α-tosylate **11d**. Alcohol **11i** (0.42 g, 1.94 mmol) yielded 0.69 g (96%) of crystalline tosylate **11j**: mp 111.0–113.0 °C (hexane); IR 1185, 1165 cm^{-1}; NMR δ 7.61–7.20 (A_2B_2, 4, J_{AB} = 8.0 Hz, H_A ortho to ester, H_B ortho to CH_3), 7.00–6.60 (m, 4, aromatic H), 4.03 (m, 1, $W_{1/2}$ = 22.0 Hz, CHOTs), 2.90–2.50 (m, 2, benzylic H), 2.42 (s, 3, tosylate CH_3), 1.10 (s, 3, CH_3); MS, m/e 370 (M^+), 198, 183 (base).

Anal. Calcd for $C_{22}H_{26}SO_3$: C, 71.32; H, 7.07. Found: C, 71.18; H, 7.10.

3α-Azido-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (11k) was prepared as described for the 3β-azide (**11f**) except the reaction temperature was 85 °C and the reaction time was 6.0 h. Tosylate **11j** (0.49 g, 0.32 mmol), after chromatography, yielded 38.8 mg of olefine **12** and 210.7 mg (63%) of azide **11k**: colorless oil; IR (film) 2100 cm^{-1}; NMR δ 7.27–6.80 (m, 4, aromatic H), 3.45 (m, 1, $W_{1/2}$ = 20.5 Hz, CHN_3), 2.93–2.63 (m, 2, benzylic H), 1.35 (s, 3, CH_3); MS, m/e 241 (M^+), 213, 198, 56 (base).

3α-Amino-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (11l). The procedure for preparing the β-amino isomer **11g** was followed. Azide **11k** (200 mg, 0.829 mmol) yielded 174 mg (97.4%) of amine **11l**: IR (film) 3380, 3300 cm^{-1}; NMR δ 7.28–6.80 (m, 4, aromatic H), 3.12–2.45 (m, 3, 2, benzylic H and 1 $CHNH_2$), 1.40 (s, 2, NH_2), 1.34 (s, 3, CH_3); MS, m/e 215 (M^+) 200, 198, 56 (base).

The picrate salt was prepared for analysis: yellow needles (H_2O): mp 214–216 °C dec.

Anal. Calcd for $C_{21}H_{24}N_4O_7$: C, 56.75; H, 5.44; N, 12.61. Found: C, 56.61; H, 5.20; N, 12.81.

3α-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aβ-octahydrophenanthrene (11c). Prepared as described for the β-dimethylamino isomer **11b**. Crude amine **11l** (162.8 mg, 0.756 mmol) provided 180.8 mg (98%) of **11c**: colorless oil; molecular distillation (95 °C (0.01 mm)) yielded 171.3 mg (93%) of **1k**; n_D 1.5438; IR (film) 2815, 2785, 1450 cm^{-1}; NMR δ 7.30–6.80 (m, 4, aromatic H), 2.92–2.62 (m, 2, benzylic H), 2.20 (s, 6, $N(CH_3)_2$), 1.36 (s, 3, CH_3); MS, m/e 243 (M^+), 228, 84 (base).

Picrate salt prepared for analysis: yellow needles (H_2O); mp 144–145 °C.

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.86. Found: C, 58.66; H, 5.90; N, 11.68.

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-3β-phenanthrol (14b). Benzoate **14a** was hydrolyzed with KOH as described for benzoate **13a**. Benzoate **14a** (0.80 g, 2.50 mmol) yielded 0.49 g (91%) of crystalline **14b**: mp 108–109 °C (hexane); IR 3665, 3420 cm^{-1}; NMR δ 7.30–6.87 (m, 4, aromatic H), 4.22 (m, 1, $W_{1/2}$ = 8.0 Hz, CHOH), 3.05–2.68 (m, 2, benzylic H), 1.28 (s, 3, CH_3); MS, m/e 216 (M^+), 201, 183 (base).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.09; H, 9.60.

4a-Methyl-1,4,4a,9,10,10aα-hexahydro-3(2*H*)-phenanthrone (14g). The Jones oxidation procedure of alcohol **14b** was identical with that of alcohol **6**. Alcohol **14b** (0.33 g, 1.53 mmol) yielded 0.30 g (91%) of crystalline ketone (**14g**): mp 80.0–81.0 °C (hexane); IR 1700 cm^{-1}; NMR δ 7.23–6.98 (m, 4, aromatic H), 3.10–2.83 (m, 2, benzylic H), 3.00 (AB quartet, 1, J_{AB} = 13.5 Hz, H-4), 2.45 (AB quartet, 1, J_{BA} = 13.5 Hz, H-4), 2.75–2.28 (m, 2, H-2), 1.11 (s, 3, CH_3); MS, m/e 214 (M^+), 199 (base).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.08; H, 8.47. Found: C, 83.92; H, 9.60.

3α-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (14f) and 3β-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (14h). Ketone **14g** was reductively aminated as described for ketone **11a**. Ketone **14g** (0.30 g, 1.40 mmol) yielded 248.7 mg (73%) of **14h** and 25.1 mg (7%) of **14f** after chromatography (10.0 g) using system A as eluent. Molecular distillation (95 °C (0.01 mm)) yielded 220.0 mg of **14h**: n_D 1.5475; IR (film) 2815, 2785 cm^{-1}; NMR δ 7.28–6.80 (m, 4, aromatic H), 2.20 (s, 6, $N(CH_3)_2$), 1.25 (s, 3, CH_3); MS, m/e 243 (M^+), 228, 198, 84 (base).

Picrate salt prepared for analysis; mp 158–159 °C (H_2O).

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.86. Found: C, 58.20; H, 6.02; N, 11.58.

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-3β-phenanthrol Tosylate (14c). Prepared as described for tosylate **11d**. Alcohol **14b** (369.4 mg, 1.71 mmol) yielded 520.0 mg (92%) of crystalline **14c**: mp 105.0–106.0 °C (hexane/ether); IR 1180, 1130 cm^{-1}; NMR δ 7.69, 7.20 (A_2B_2, 4, J_{AB} = 8.0, H_A ortho to ester, H_B ortho to CH_3), 4.85 (m, 1, $W_{1/2}$ = 8.0, Hz, CHOTs), 2.97–2.55 (m, 2, benzylic H), 2.41 (s, 3, tosylate CH_3), 1.17 (s, 3, CH_3); MS, m/e 370 (M^+), 198, 183 (base).

Anal. Calcd for $C_{22}H_{26}SO_3$: C, 71.32; H, 7.07. Found: C, 71.65; H, 7.19.

3α-Azido-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (14d) was prepared as described for azide **11f** except the reaction temperature was 75 °C and the reaction time was 5.0 h. Tosylate **14c** (200.0 mg, 0.541 mmol) yielded 20.5 mg of olefins **15** and **16** and 85.5 mg (66%) of azide **14d**: colorless oil; IR (film) 2100 cm^{-1}; NMR δ 7.28–6.86 (m, 4, aromatic H), 3.51 (m, 1, $W_{1/2}$ = 210 Hz, CHN_3), 1.05 (s, 3, CH_3); MS, m/e 241 (M^+), 213, 198, 83 (base).

3α-Amino-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (14e) was prepared as described for amine **11g**. Curde azide **14d** (85.5 mg, 0.355 mmol) yielded 74.0 mg (97%) of amine **14e**: colorless oil; IR (film) 3378, 3300 cm^{-1}; NMR δ 7.30–6.88 (m, 4, aromatic H), 3.22–2.20 (m, 4), 1.58 (s, 3, NH_2), 1.06 (s, 3, CH_3); MS, m/e 215 (M^+), 200, 198, 56 (base).

The picrate salt was prepared for analysis: yellow needles (H_2O); mp 208–209 °C.

Anal. Calcd for $C_{21}H_{24}N_4O_7$: C, 56.75; H, 5.44; N, 12.61. Found: C, 56.80; H, 5.31; N, 12.40.

3α-(*N*,*N*-Dimethylamino)-4a-methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (14f) was prepared as described for dimethylamine **11b**. Crude amine **14e** (74.0 mg, 0.344 mmol) yielded 83.0 mg (99%) of **14f** as a clear oil. Molecular distillation

(95 °C (0.03 mm)) provided 75.0 mg of **14f**: n_D 1.5483; IR 2815, 2785 cm^{-1}; NMR δ 7.28–6.80 (m, 4, aromatic H), 2.28 (s, 6, N-$(CH_3)_2$), 1.05 (s, 3, CH_3); MS, *m/e* 243 (M^+), 228, 198, 84 (base).

Picrate salt prepared for analysis: yellow needles (H_2O); mp 151–152 °C.

Anal. Calcd for $C_{23}H_{28}N_4O_7$: C, 58.47; H, 5.97; N, 11.85. Found: C, 58.57; H, 5.98; N, 11.46.

3,4aα-Oxymethano-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (18a) and 3,4aβ-Oxycarbonyl-1,2,3,4,4a,9,-10,10aα-octahydrophenanthrene (18b). The apparatus consisted of a Pyrex water-jacketed sublimation apparatus in which the cold finger had been replaced with a positive pressure gas adaptor. This setup was placed in a Hanovia photochemical reactor which contained eight 3000 Å high pressure mercury arc lamps. The internal temperature of the reaction was high enough to maintain refluxing benzene without any additional heat source.

Alcohol **14b** (50.0 mg, 0.231 mmol) in dry benzene (20 mL) was photolyzed with $Pb(OAc)_4$ (307.9 mg, 0.695 mmol, previously dried overnight in vacuo over potassium hydroxide and calcium chloride) and I_2 (176.4 mg, 0.695 mmol) for 6 h with constant stirring at reflux. The reaction mixture was cooled, H_2O was added, and the mixture was extracted with ether (3 × 25 mL). The combined ether extracts were washed with H_2O, dried, and evaporated to yield 53.0 mg of an oil. Preparative TLC (2 mm) with $CHCl_3$ as eluent yielded 31.5 mg of an oily solid. Crystallization from cyclohexane yielded 18.0 mg of **18b** with the mother liquor (12.0 mg) enriched in **18a**. Lactone **18b**: mp 129–130 °C (cyclohexane); IR 1768 and 1120 cm^{-1}; NMR δ 7.20–7.05 (m, 4, aromatic H), 4.91 (m, 1, $W_{1/2}$ = 11 Hz, C_3 methine H), 3.22–2.68 (m, 3), 2.28–1.40 (m, 8); MS, *m/e* 228 (M^+), 184 (base), 141. Ether **18a**: clear oil; IR 1040 cm^{-1}; NMR δ 7.31–6.88 (m, 4), aromatic HO, 4.88 (m, 1, $W_{1/2}$ = 11 Hz, C_3 methine H), 4.05–3.58 (d, 2, J = 8.0 Hz, H of C_{4a} methylene). 3.58 (d, 1), 3.00–2.40 (m, 3 H), 2.10–1.32 (m, 8 H); MS, *m/e* 214 (M^+), 184, 86, 84 (base).

General Procedure for Deuterium Exchange Studies. Ketone **14g** (50.0 mg, 0.234 mmol) in a solution of CH_3OD/D_2O (9:1) containing KOH (25 mg) was stirred at 25 °C for 2 days. The mixture was concentrated in vacuo, and the residue was taken up in ether and filtered to afford 50.0 mg of exchanged product as a colorless oil: IR 2220 cm^{-1}; NMR δ 7.30–6.88 (m, 4, aromatic H), 3.00–2.65 (m, 2, benzylic H), 2.25–1.50 (m, 5 H), 1.31 (s, 3, CH_3); MS, *m/e* 218 (M^+), 83 (base).

4a-Methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene (9e). The ethylenethiolketal of ketone **14g** was prepared according to the method of L. F. Fieser.[32] To Ketone **14g** (50.0 mg, 0.23 mmol) was added 0.4 mL of ethanedithiol and 0.4 mL of boron trifluoride etherate. This yellow mixture was stirred at 25 °C for 3 h then poured onto cold 10% KOH (5 mL). The aqueous base was saturated with NaCl and extracted with ether to yield 40.5 mg (60%) of a yellow oil which contained no carbonyl absorption in the infrared spectrum. This crude oil was added to 20 mL of refluxing EtOH containing one teaspoon of Raney nickel freshly prepared according to the method of Burgstahler.[33] Desulfurization was complete in 20 min. Removal of the catalyst by filtration followed by evaporation of the solvent in vacuo yielded 26.0 mg (93%) of crude **9e**. Preparative TLC (0.5 mm) with hexane as eluent provided pure **9e**. The NMR spectrum was identical with that reported by E. Wenkert and co-workers.[22]

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Registry No. 1, 1686-50-6; 2, 70524-91-3; 3, 6606-34-4; 4, 70550-22-0; 5, 22139-44-2; 6, 70524-73-1; 8, 70550-23-1; **9a**, 70524-87-7; **9b**, 70524-88-8; **9c**, 70524-89-9; **9c** methiodide, 70550-24-2; **9d**, 70524-90-2; **9d** methiodide, 70550-25-3; **9e**, 70561-39-6; **10a**, 70524-92-4; **10b**, 70524-93-5; **10c**, 70524-94-6; **10d**, 70524-95-7; **11a**, 70550-26-4; **11b**, 70524-86-6; **11b** picrate, 70550-27-5; **11c**, 70524-85-5; **11c** picrate, 70550-28-6; **11d**, 70524-78-6; **11e**, 70524-77-5; **11f**, 70524-82-2; **11g**, 70524-84-4; **11g** picrate, 70550-29-7; **11h**, 70524-76-4; **11i**, 70524-74-2; **11j**, 70524-79-7; **11k**, 70524-81-1; **11l**, 70524-83-3; **12**, 70550-30-0; **13a**, 70550-31-1; **13b**, 70550-32-2; **14a**, 70524-67-3; **14b**, 70524-65-1; **14c**, 70524-68-4; **14d**, 70524-69-5; **14e**, 70524-70-8; **14e** picrate, 70550-33-3; **14f**, 70524-71-9; **14f** picrate, 70550-34-4; **14g**, 70550-35-5; **14h**, 70524-72-0; **14h** picrate, 70613-68-2; **15**, 30630-62-7; **16**, 70550-36-6; **18a**, 70550-37-7; **18b**, 70562-44-6; 4a-methyl-4,4a,9,10-tetrahydrophenanthrene, 70550-38-8; phenanthrene, 85-01-8.

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