3,17β-Diacetoxy-5α-androsta-1,3-diene (2). Using Reagent b.—Two hundred milligrams of 17β-acetoxy-5α-androst-1-en-3-one (1) was dissolved in 20 ml of reagent b and the mixture was allowed to stand at room temperature. After 10 min a sample was taken for tlc and the chromatogram showed that the major components in the reaction mixture were compounds 1 and 2, with a small amount of 4. The mixture was worked up as described previously and the residue (180 mg) was chromatographed on silica gel. The first compound eluted from the column was enol acetate 2 (40 mg, 18%). When this substance was recrystallized twice from methanol containing a trace of pyridine, it had a melting point, mixture melting point, and infrared spec identical with those of an authentic sample. The remainder of the material eluted from the column consisted of starting material 1 and a small amount of 4.

Using Reagent a.—When 200 mg of unsaturated ketone 1, dissolved in 20 ml of reagent a, was allowed to stand at room temperature for 10 min and then worked up as described previously, 175 mg of residual products was obtained. This was chromatographed on silica gel, whereby 43 mg (19%) of enol acetate 2, mp 134–136°, was obtained. A recrystallization from methanol containing a trace of pyridine raised the melting point to 139–140°. The remainder of the material recovered was unchanged starting ketone 1.

4-Methylestra-1,3,5(10)-triene-1,17β-diol Diacetate (3).—A solution of 100 mg of 17β-acetoxyandrosta-1,4-dien-3-one (8) in 10 ml of reagent b was allowed to stand at room temperature for 30 min. The reaction mixture was washed with saturated sodium carbonate solution and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue (95 mg) was recrystallized from acetone–hexane, yielding 85 mg of rearranged diacetate 3, mp 134–136° (lit.[24] mp 134–135°).

17β-Hydroxy-5α-androst-1-en-3-one (7).—A solution of 35 mg of diketone 4 in 10 ml of 15% methanolic potassium hydroxide was allowed to stand at room temperature for 30 min. The mixture was diluted with water and extracted with ether. The ether extracts were washed with dilute hydrochloric acid and then with water, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left 20 mg of product which crystallized from methanol. This substance appears to have a double melting point but the lower one could not be definitely established; the higher one was at 152–154° (lit.[26] mp 150°). When ketone 1 was treated in the manner described above, the same product was obtained, as determined by a comparison of their identical infrared spectra and melting points, as well as an undepressed mixture melting point.

Compound 7 was allowed to react for 20 min with reagent b at room temperature. After this time, tlc showed that the major product in the mixture was 1, together with a small amount of enol acetate 2.

4α-Acetyl-17β-acetoxy-5α-androst-1-en-3-one (4) from 3,17β-Diacetoxy-4-acetyl-5α-androsta-1,3-diene (5).—A solution of 20 mg of enol acetate 5 in 7 ml of 5% hydrochloric acid in methanol was allowed to stand at room temperature for 30 min. The reaction mixture was diluted with water and extracted with ether, and the ether extracts were washed with sodium carbonate solution. The ether layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The remaining product (15 mg) was recrystallized from acetone–hexane and identified as diketone 4 by its melting point (198–200°), undepressed mixture melting point, and its infrared spectrum.

The Thin Layer Chromatographic Experiments.—For the time study shown in Figure 2, 1.00 mg of each of compounds 1, 2, 4, and 5 was allowed to react with 0.100 ml of reagent b at room temperature. After the indicated time intervals, the reaction mixtures were spotted in equivalent quantities on 8.5 × 11 cm glass plates coated with silica gel,[20] and the plates were eluted with an acetone (7 ml)–hexane (30 ml) mixture. The plates were dried in an oven at 100° for 10 min, then developed by spraying with chlorosulfonic acid, and again dried at 100° for 1 hr.

The tlc method was calibrated to give semiquantitative, as well as qualitative results. For the semiquantitative calibration chromatograms, 1.00 mg of each of compounds 1, 2, 4, and 5 was dissolved in 0.100 ml of acetone at room temperature. Silica gel coated plates were then spotted, eluted, and developed as described above. The densities of the spots corresponding to the four compounds were identical on visual inspection.

Registry No.—1, 64-82-4; 2, 3941-70-6; 3, 6224-00-6; 4, 10050-97-2; 5, 10050-96-1.

(26) A. Butenandt and H. Dannenberg, *Chem. Ber.*, **73**, 206 (1940).

Cassaine Analogs. I. Intermediate Hydrophenanthrones

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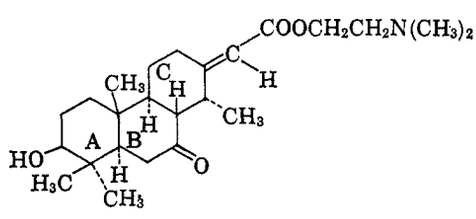
7-Methoxytetrahydrophenanthrone (5) was used to prepare tricyclic ketones required for the synthesis of cassaine analogs. All four possible ring-A-aromatic 7-methoxyoctahydrophenanthrols were prepared, as well as perhydrophenanthrones having *cis-anti-trans*, *trans-anti-cis*, and *trans-anti-trans* configurations.

For years it has been known that the *Erythrophleum* alkaloid cassaine (1) exerts an effect on the heart similar to that of the cardiac glycosides.[1] Recently, Turner, Buchardt, Herzog, Morin, Riebel, and Sanders[2] reported the total synthesis of this complex molecule. Hauth, Stauffacher, Nicklaus, and Melera[3] and, more recently, Clarke, Daum, Shaw, and Kullnig[4] have contributed some additional data to certain aspects of configuration which have more rigorously defined the structure of cassaine.



1

It was of interest to determine the effect of various changes in configuration and functional groups of cassaine on its biological activity. This paper is devoted to the synthesis of several tricyclic ketones which were subsequently[5] converted to basic ester analogs of cassaine. A carbonyl group in ring C was essential for attaching the required side chain.

(1) See F. Erjavec and Š. Adamič, *Arch. Intern. Pharmacodyn.*, **155**, 251 (1965); E. L. McCawley in "The Alkaloids," Vol. V, R. H. F. Manske, Ed., Academic Press Inc., New York, N. Y., 1955, pp 101–107 and references therein.

(2) R. B. Turner, O. Buchardt, E. Herzog, R. B. Morin, A. Riebel, and J. M. Sanders, *J. Am. Chem. Soc.*, **88**, 1766 (1966).

(3) H. Hauth, D. Stauffacher, P. Nicklaus, and A. Melera, *Helv. Chim. Acta*, **48**, 1087 (1965).

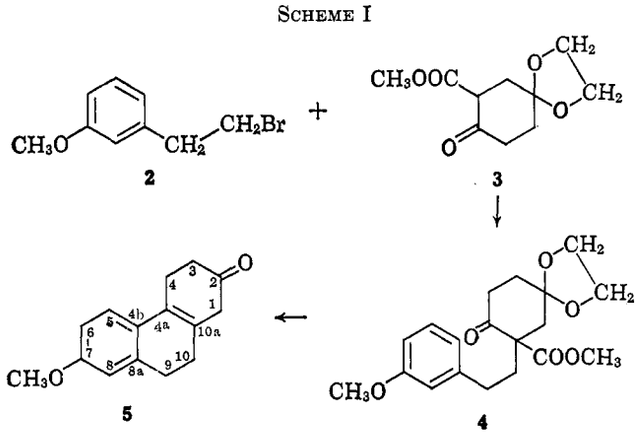
(4) R. L. Clarke, S. J. Daum, P. E. Shaw, and R. K. Kullnig, *J. Am. Chem. Soc.*, **88**, 5865 (1966).

(5) R. L. Clarke, S. J. Daum, and P. E. Shaw, *J. Med. Chem.*, in press.

Tetrahydrophenanthrone **5**[6] appeared to be an exceptionally suitable intermediate for the synthesis of cassaine analogs, in that it allows the controlled introduction of hydrogen at positions 4a, 4b, 8a, and 10a to give all possible configurations at the ring junctions. At the same time, the lack of angular methyl substitution gives the molecule a symmetry about an axis through ring B that permits the interchangability of the 2 and 7 positions.

In the course of their work on the total synthesis of steroids, Nagata, Hirai, Terasawa, and Kikkawa[6] prepared tetrahydrophenanthrone **5** by condensation of methyl vinyl ketone with 6-methoxy-2-tetralone. Since this tetralone is not conveniently prepared and since condensation reactions with methyl vinyl ketone are not very satisfactory, we investigated another route to compound **5**. Keto ester **3**,[7] which can be readily prepared from furfural, was alkylated with *m*-methoxyphenethyl bromide (**2**) to afford keto ester **4**. Treatment of compound **4** with sulfuric acid in dioxane not only hydrolyzed the ketal and ester groups, but also effected decarboxylation and cyclization to produce tetrahydrophenanthrone **5**. (See Scheme I.) This route offered no advantages over the Japanese method.[6]

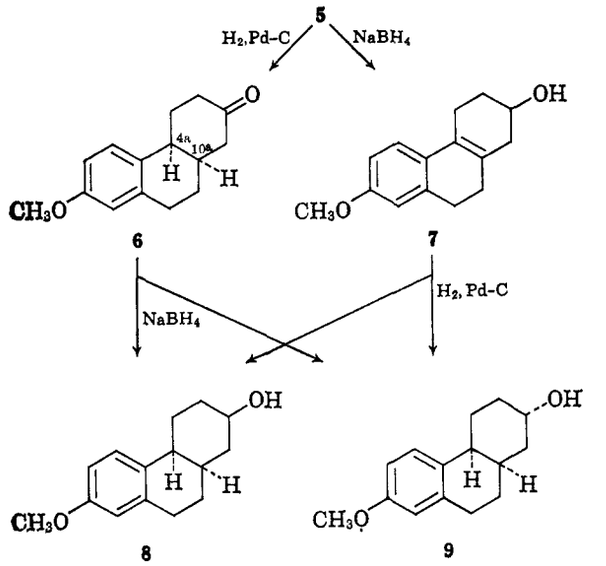
SCHEME I



Low-pressure hydrogenation of compound **5** with palladium-on-carbon catalyst gave the hexahydro compound **6**[8] with hydrogens at centers 4a and 10a in a *cis* relationship. Reduction of **5** with sodium borohydride in ethanol afforded the phenanthrol **7**, which upon low-pressure hydrogenation with palladium-on-carbon catalyst, allowed for the isolation of two isomers **8** and **9**, formed in the approximate ratio 7:2. (See Scheme II.)

Compound **7**, being essentially flat, can approach the catalyst from either direction. On the basis of approach to the catalyst it would be difficult to predict whether there is a directive effect owing to absorption of the hydroxyl group onto the catalytic surface[9] or whether the direction of hydrogenation is controlled by a steric effect.[10]

SCHEME II



Reduction of **6** with sodium borohydride gave compounds **8** and **9** in the approximate ratio 3:1. This ratio is probably determined by steric control of approach by borohydride in this *cis*-fused β-decalone system.[11] On this basis, compound **8**, the major product of both the sodium borohydride reduction of **6** and the catalytic hydrogenation of **7**, can be assigned the configuration with the 2-hydroxyl group *trans* to the hydrogens at positions 4a and 10a. The following transformations (Scheme III) afford further chemical evidence for the configurational assignments in **8** and **9** as well as making available ketones needed for the cassaine studies.

Reduction (Li–NH_3) of the major isomer **8** and hydrolysis of the resulting enol ether afforded compound **10**. Formation of the tetrahydropyranyl ether of **10** and reduction (Li–NH_3) gave a product (**11**) which was not characterized but was acetylated and treated with acid to give the diol monoacetate **12**. Oxidation with chromium trioxide–pyridine gave compound **13** which was saponified without further purification to yield hydroxy ketone **14**. Reduction (Li–NH_3) of **14** afforded a diol (**15**) which was identical by infrared spectral comparison, thin layer chromatography (tlc), gas–liquid partition chromatography (glpc), and melting point with the diol obtained by reduction (Li–NH_3) of **10** or saponification of **12**.

Of the two alcohols epimeric at C-2 which could have been produced, the α form must either bear an axial conformation or, in being equatorial, force ring B into an unfavorable configuration. These considerations make this isomer quite unlikely to be produced, especially since the β epimer is thermodynamically much more favorable. A single product was isolated in good yield and the equatorial character of its hydroxyl group is supported by spectral evidence described below. The configurational assignment in **15**, in turn, determines the configuration in **8** and is in accord with the earlier evidence for **8**.

One further configurational detail, the *trans vs. cis* relationship between the hydrogens at 4a and 4b of **14** and **15**, needs support. Catalytic hydrogenation of

(6) W. Nagata, S. Hirai, T. Terasawa, and I. Kekkawa, *Chem. Pharm. Bull.* (Tokyo), **9**, 756 (1961).

(7) R. M. Lukes, G. I. Poos, and L. H. Sarett, *J. Am. Chem. Soc.*, **74**, 1401 (1952).

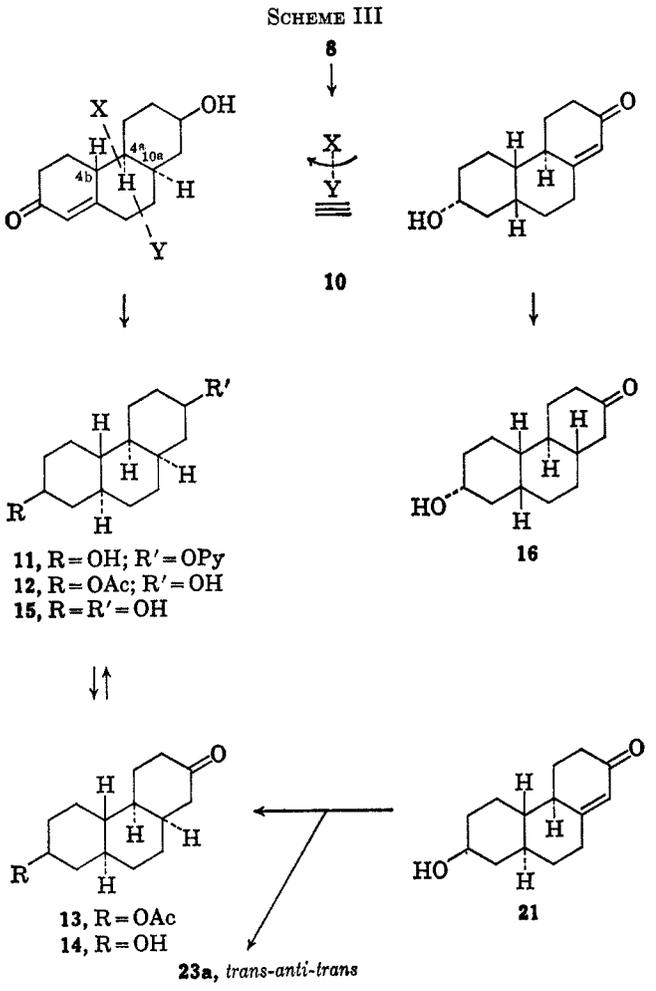
(8) W. Nagata, T. Teresawa, and K. Tori, *ibid.*, **86**, 3746 (1964). Mention is made of this compound without description.

(9) (a) T. J. Howard, *Chem. Ind.* (London), 1899 (1963); (b) S. Nishimura and K. Mori, *Bull. Chem. Soc. Japan*, **36**, 318 (1963); (c) T. J. Howard, *Rec. Trav. Chim.*, **83**, 992 (1964); (d) S. Mitsui, Y. Senda, and H. Saito, *Bull. Chem. Soc. Japan*, **39**, 694 (1966).

(10) R. L. Burwell, *Chem. Rev.*, **57**, 895 (1957).

(11) R. L. Clarke and C. M. Martini, *J. Am. Chem. Soc.*, **81**, 5716 (1959).

SCHEME III



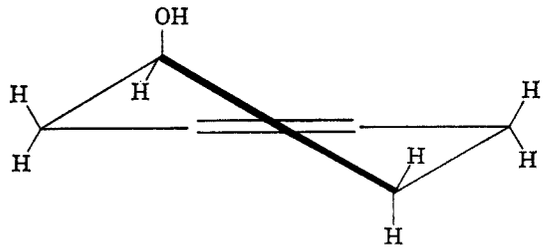


Figure 1.

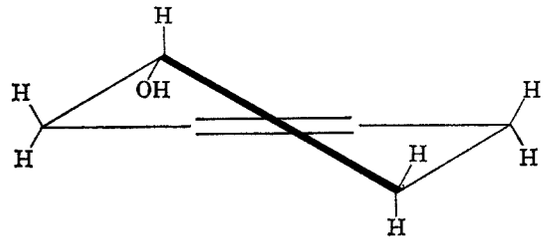


Figure 2.

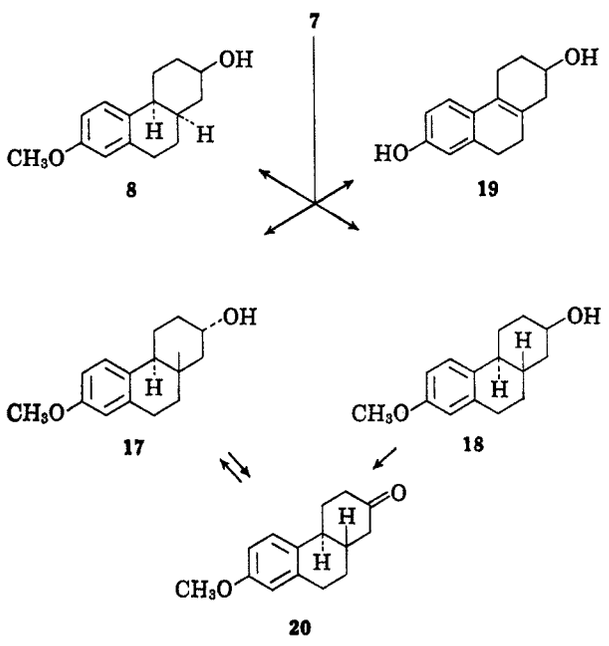
the double bond of **21** (4b and 4a hydrogens *trans*, see below) produced isomer **14** together with the *trans-anti-trans* isomer **23a** and thereby settled this point.

Now that the configurations of the products **8** and **9** from catalytic hydrogenation of **7** are known, it is possible to make further comment on the guiding factors involved. If only steric effects are considered, the degree of selectivity in the hydrogenation can be predicted. Two conformations of **7** must be considered; the differences are shown in Figures 1 and 2. The populations of these conformations can be considered to be approximately equal since the difference in energy is small.[12] In the conformation shown in Figure 1, approach to the catalyst surface would occur from the side opposite to the hydroxyl group. In the conformation shown in Figure 2, approach to the catalytic surface would occur from either side. Therefore, the side opposite from the hydroxyl group is favored and the actual course of the hydrogenation follows predictions based upon steric grounds alone.

An A/B-*cis* ring-C ketone, compound **16**, was produced when compound **10** was treated with lithium in ammonia in the absence of alcohol. It is interesting here to note that the only difference between **14** and **16** lies in the oxidation states of positions 2 and 7.

Now that ring-C ketones with *trans-anti-cis* and *cis-anti-trans* configurations had been made, it was desirable to make ketones with a *trans-anti-trans* ring configuration, the configuration of cassaine. Reduction of **7** ($Na-NH_3$) produced four products (**17**, **18**, **8**, **19**, Scheme IV). Two of these monools had to be B/C-*trans*-2-ols since both B/C-*cis*-2-ols have already been described and, indeed, one of them (**8**) was isolated from this reaction (3.8%). The B/C-*trans*-2β-ol **18** (7.5%, axial hydroxyl) was recognizable since oxidation of it to **20** followed by reduction with sodium borohydride gave mostly (7:3) the major product from the reduction of **7** (51%), *trans*-2α-ol **17** (equatorial OH). Interestingly, 10% of phenolic compound **19** was produced by hydrogenolysis during the chemical reduction of **7**.

SCHEME IV



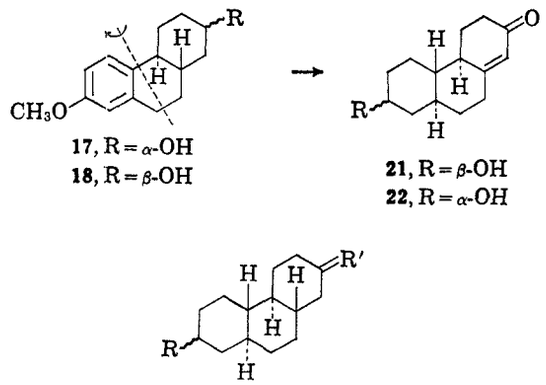
The infrared spectral data support[13] the expectation that only one (**18**) of the four isomers **8**, **9**, **17**, and **18** has an axial hydroxyl group (see the Experimental Section).

(12) E. L. Eliel in "Stereochemistry of Carbon Compounds," McGraw-Hill Series in Advanced Chemistry, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 234–240, and references therein.

(13) (a) A. R. H. Cole, R. N. Jones, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 5571 (1952); (b) A. R. H. Cole, *J. Chem. Soc.*, 4969 (1952); (c) H. S. Aaron and C. P. Rader, *J. Am. Chem. Soc.*, **85**, 3046 (1963).

Reduction of **17** ($Li-NH_3$) followed by acid hydrolysis of the resulting enol ether afforded the unsaturated ketone **21**. In a similar fashion, reduction ($Li-NH_3$) of compound **18** afforded the unsaturated ketone **22**. (See Scheme V.) Reduction ($Li-NH_3$) of **21** and **22**

SCHEME V



17, R = α-OH
18, R = β-OH

21, R = β-OH
22, R = α-OH

23a, R = β-OH; R′ = O
b, R = β-OH; R′ = H, α-OH
c, R = β-OH; R′ = N—N—C—NH_2·HCl (H; NH)
d, R = β-OH; R′ = 1,3-dithiolane
e, R = α-OH; R′ = O

24a, R = R′ = O
b, R = R′ = N—N—C—NH_2·HCl (H; NH)
c, R = O; R′ = 1,3-dithiolane

25

gave compounds **23a** and **23e**, respectively. The amidinohydrazone derivative **23c** as well as the thioketal derivative **23d** were prepared from **23a**.

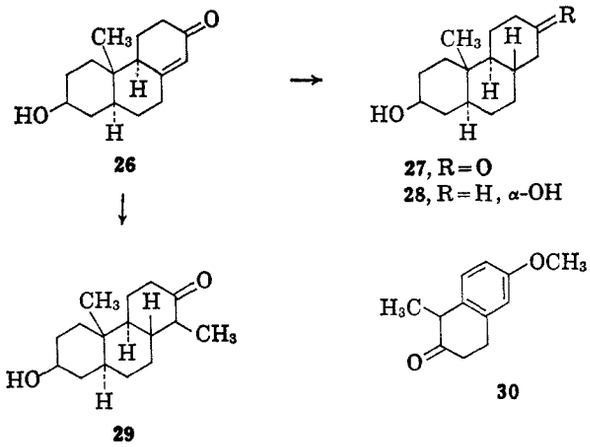
Oxidation of **23b** with chromium trioxide–pyridine afforded the diketone **24a** from which the bisamidinohydrazone derivative **24b** was prepared. Oxidation of **23d** and **21** with chromium trioxide in pyridine afforded compounds **24c** and **25**, respectively.

The following compounds, containing a 4bβ-methyl group, were also prepared. Reduction ($Li-NH_3$) of unsaturated ketone **26**[14a] gave compounds **27** and **28**. (See Scheme VI.) Reductive alkylation by the Stork, Rosen, and Goldman procedure[14b] afforded compound **29**. Tetralone **30**, an intermediate in the preparation of **26**, was obtained for the first time in crystalline form, mp 45.5–47°.

Experimental Section[15]

dl-**2-Carbomethoxy-2-(*m*-methoxyphenethyl)cyclohexane-1,4-dione 4-Ethylene Ketal (4).**—A solution of 5.33 g (0.047 mole) of potassium *t*-butoxide in 100 ml of *t*-butyl alcohol was stirred

SCHEME VI



26

27, R = O
28, R = H, α-OH

29

30

while 10.0 g (0.047 mole) of 2-carbomethoxycyclohexane-1,4-dione 4-ethylene ketal (**3**)[7] in 150 ml of *t*-butyl alcohol was added. An additional 100 ml of *t*-butyl alcohol was added, followed by 10 g (0.047 mole) of *m*-methoxyphenethyl bromide (**5**). The suspension was refluxed while being stirred mechanically for 72 hr. At this point the reaction mixture was slightly alkaline to pH paper.

The cooled reaction mixture was added to ice water. Ether was added followed by dilute hydrochloric acid. The layers were separated and the ether layer was washed with a saturated sodium bicarbonate solution. The ether was extracted twice with 200-ml portions of 5% potassium hydroxide. This alkaline solution, upon acidification with hydrochloric acid, yielded 1.45 g of starting 2-carbomethoxycyclohexane-1,4-dione 4-ethylene ketal which was identified by its melting point.

The ether solution from which the starting material had been removed was then washed with ice cold, dilute hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride. After the ether solution was dried (Na_2SO_4), the solvent was removed to leave a yellow, viscous oil. This residue was distilled and a fraction that boiled at 190–205° (0.08–0.15 mm) was collected (10.1 g of colorless, viscous oil, 62%): infrared absorption ($CHCl_3$) at 5.84 (s, broad), 6.25, 6.32 μ (m); nmr spectrum ($CDCl_3$) peaks at δ = 7.0–7.8 (4 H, aromatic), 4.5, 4.3, 4.2 (10 H, 2 methyl and ketal), and 2.0–4.1 ppm (10 H, aliphatic). The analytical sample, prepared in an identical experiment, boiled at 195–196° (0.18–0.20 mm);[4f] $n^{25}D$ 1.5267.

Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.52; H, 6.94. Found: C, 65.4; H, 6.9.

3,4,9,10-Tetrahydro-7-methoxy-2(1H)-phenanthrone (5).[6]—Sulfuric acid (1 l., 11 *N*) was added all at once to a solution containing 115.4 g (0.33 mole) of ketal **4** in 1 l. of dioxane. The reaction mixture was stirred at 100° in a nitrogen atmosphere for 4.5 hr. The cooled solution was poured into ice and enough water was added to bring the total volume to 3 l. The aqueous mixture was extracted with ether several times. The combined ether layers were washed with 10% sodium carbonate and finally with saturated sodium chloride solution. The ether solution was dried (Na_2SO_4) and concentrated by warming *in vacuo* to afford 73.9 g of a red oil: λ_{max}^{EtOH} 273 mμ (ε 13,000) [lit.[6] λ_{max} 273 mμ (ε 16,100)]. This material was chromatographed on 2 kg of silica gel. Elution with 4 l. of ether–pentane (1:9) and 20 l. of ether–pentane (1:3) removed less-polar material. Continued elution with 5.5 l. of ether–pentane (1:3) afforded 18.2 g of an oil which crystallized from ether containing hexane to give 16.5 g of crystals of compound **5**, mp 75–77° (lit.[6] mp 78.0–78.5°). Further elution (5 l.) gave another 17.2 g of oil which resulted in 14.8 g of a second crop of crystals, mp 72–75°. Upon continued elution a third crop (3 g, mp 66–74°) was also obtained (yield 46%). This material was of sufficient purity to use in later experiments.

(14) (a) W. Nagata, T. Terasawa, and T. Aoki, *Tetrahedron Letters*, 865 (1963); (b) G. Stork, P. Rosen, and N. L. Goldman, *J. Am. Chem. Soc.*, **83**, 2965 (1961).

(15) All melting points are corrected. The infrared spectra were recorded on a Perkin-Elmer infrared spectrophotometer, Model 21, unless otherwise noted. The ultraviolet spectra were recorded on a Cary spectrophotometer, Model 15. The nmr spectra were recorded on a Varian A-60 nmr spectrometer. Solutions (10–20%) were used with TMS as an internal standard (TMS = 0 ppm). Silica gel G, purchased from Brinkmann Instruments, Inc., was used for thin layer chromatography.

Catalytic Hydrogenation of 3,4,9,10-Tetrahydro-7-methoxy-2(1H)-phenanthrone (5).[6]—A solution of 1 g (4.4 mmoles) of phenanthrone **5** in 300 ml of ethyl acetate was hydrogenated at a pressure of 3.86 kg/cm² and room temperature in the presence of 100 mg of 10% palladium-on-carbon catalyst. After 1 hr the hydrogenation was complete and the catalyst was removed by filtration through Supercel. The solvent was removed by warming *in vacuo* and the residue was crystallized from ether containing hexane to yield 900 mg of *dl*-**3,4,4aα,9,10,10aα-hexahydro-7-methoxy-2(1H)-phenanthrone** (**6**), mp 92–93°, and a second crop (100 mg), mp 89–91° (yield quantitative). The analytical sample, from ether containing hexane, melted at 92.5–93°.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.88. Found: C, 78.4; H, 8.0.

dl-**1,2,3,4,9,10-Hexahydro-7-methoxy-2-phenanthrol** (**7**).—A solution of 36.7 g (0.16 mole) of ketone **5** in 1500 ml of 95% ethanol was treated with 19 g of sodium borohydride in 150 ml of water. After 3 hr at room temperature, acetone was added to the reaction mixture to decompose the excess borohydride. The volume was reduced to about 400 ml by warming *in vacuo*. Water and ether were added and the layers were separated. The ether was washed with saturated sodium chloride solution. The aqueous layers were washed again with fresh ether and the organic layers were then combined. The ether solution was dried (Na_2SO_4) and the solvent was removed leaving behind an oily residue (36.1 g). Crystallization from ether containing hexane gave a crop (20.3 g), mp 93–94°. Further concentration of the mother liquor afforded another 9.3 g (81%) of **7**, mp 90–92°. The analytical sample obtained from a similar experiment had mp 92–93°; λ_{max}^{EtOH} 272 mμ (ε 16,400); λ_{max}^{KBr} 3.10 (s), 6.07 (w), 6.24 (m), and 6.35 μ (w).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.24; H, 7.88. Found: C, C, 78.1; H, 7.7.

The identical compound **7** was obtained when ketone **5** was prepared by the procedure employed by Nagata, *et al.*[6]

Catalytic Hydrogenation of *dl*-1,2,3,4,9,10-Hexahydro-7-methoxy-2-phenanthrol (**7**).—A solution of 15 g (0.066 mole) of phenanthrol **7** in 300 ml of ethyl acetate was hydrogenated at a pressure of 3.86 kg/cm² and room temperature in the presence of 1.5 g of 10% palladium-on-carbon catalyst. After 0.75 hr the hydrogenation was complete. The catalyst was removed by filtration through Supercel and the filtrate was combined with the filtrate of an identical experiment. The solvent was removed by warming *in vacuo* to leave 31.5 g of an oily residue which crystallized from ether containing hexane. Recrystallization of this material from ether containing hexane afforded 13.6 g of solid, mp 80–83°.

The mother liquor was chromatographed on 1.5 kg of silica gel. The course of the elution was followed by thin layer chromatography (tlc). Elution with 13 l. of ether–pentane (1:1) removed some less polar material. Continued elution with 5.5 l. of solvent of the same concentration afforded 6 g of material which, on crystallization from ether containing hexane, yielded 4.83 g of solid, mp 84–87°, and 0.4 g of solid, mp 81–85°. Tlc indicated that these crops had the same R_f value as the solid obtained by direct crystallization. Combination and recrystallization from ether containing hexane afforded 16.1 g of *dl*-**1,2,3,4,4aα,9,10,10aα-octahydro-7-methoxy-2β-phenanthrol** (**8**), mp 84–88°. The mother liquor, on concentration, afforded another 2 g of **8**, mp 80–83° (yield 61%). Tlc showed a single spot (silica gel; developing solvent, ether; R_f 0.37). The analytical sample, from ether containing hexane, melted at 84–88°; infrared absorption (KBr) 9.60 μ (s) and (CCl_4) 2.76 μ[16] (3625 cm^{-1}, with half band width ≈23 cm^{-1}).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.57; H, 8.68. Found: C, 77.4; H, 8.6.

This compound apparently shows polymorphism. Recrystallization of the analytical sample from ether containing hexane gave material melting at 77–82°. The infrared spectrum in solution was identical with that of the higher melting material. Tlc analysis showed no difference in purity or position of spot. Afterward, we could not obtain the higher melting polymorph.

Further elution in the above-described chromatography with 2.5 l. of ether–pentane (1:1) gave 4.2 g of a mixture of two compounds (tlc analysis). Finally, elution with another 4 l. of the same solvent mixture gave an oily residue which crystallized from ether containing hexane and afforded 5.3 g of crude *dl*-**1,2,3,4,-4aα,9,10,10aα-octahydro-7-methoxy-2α-phenanthrol** (**9**), mp 67–70°. Recrystallization from ether containing hexane gave 5 g of **9**, mp 89–90.5° (yield 17%). Tlc analysis showed a single spot (silica gel; developing solvent, ether; R_f 0.31).

The analytical sample, from ether containing hexane, melted at 88–90°; infrared absorption (KBr) 9.60 and 9.50 μ and (CCl_4) 2.76 μ[16] (3627 cm^{-1} with half band width ≈19 cm^{-1}).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.57; H, 8.68. Found: C, 77.3; H, 8.5.

Sodium Borohydride Reduction of *dl*-3,4,4aα,9,10,10aα-Hexahydro-7-methoxy-2(1H)-phenanthrone (**6**).[8]—A solution of 580 mg (2.5 mmoles) of **6** in 25 ml of absolute ethanol was treated with 240 mg of sodium borohydride in 2.5 ml of water. After the reaction mixture sat at room temperature overnight, the excess borohydride was decomposed by adding acetone followed by water. The reaction mixture was washed with ether and the ether was washed with saturated sodium chloride solution. The ether was dried (Na_2SO_4) and evaporated to leave 500 mg of oily residue. Tlc of the crude product indicated that a major (less polar) material corresponded to **8** and a minor (more polar) material corresponded to **9**.

The oily residue was chromatographed on silica gel coated plates (Brinkmann PF_{254}) which were developed with ether–pentane (3:1). About 170 mg of residue was put on each of three plates (20 × 40 cm) carrying a 1-mm coating of silica gel. The major band from the plates (less polar) afforded 310 mg (54%) of **8**, which was identified by melting point, infrared spectrum, and tlc analysis. The more polar band afforded 110 mg (19%) of **9** which was identified by melting point, infrared spectrum, and tlc analysis.

dl-**4,4aα,4bβ,5,6,7,8,8aβ,9,10-Decahydro-7α-hydroxy-2(3H)-phenanthrone** (**10**).—A solution of 11 g (0.05 mole) of phenanthrol **8** in 200 ml of tetrahydrofuran and 200 ml of *t*-butyl alcohol[17] was added to 400 ml of ammonia. Lithium (5.5 g, 0.79 g-atom) was added to the stirred solution over a 2-hr period. The reaction mixture, which never became blue but developed a bronze layer, was stirred for an additional 4 hr. At the end of this time the reaction mixture appeared cloudy and white. Methanol (60 ml) was added and the ammonia was evaporated. Water and ether were added, the mixture was shaken, and the layers were separated. The ether layer was washed twice with saturated sodium chloride solution. The aqueous layers were washed with a fresh portion of ether and the ether layers were combined, dried (Na_2SO_4), and concentrated by warming *in vacuo*. The syrupy residue was dissolved in 150 ml of dioxane. The dioxane solution was treated with 75 ml of 2 *N* hydrochloric acid and heated in a nitrogen atmosphere on a steam bath for 0.5 hr. Saturated sodium chloride solution and ether were added to the cooled reaction mixture; it was shaken and the layers were separated. The ether was washed again with saturated sodium chloride solution. The aqueous layers were washed again with a fresh portion of ether. The combined ether layers were dried (Na_2SO_4) and concentrated by warming *in vacuo* to leave 11 g of an oily residue.

Crystallization from acetone afforded 5.36 g of **10** [mp 148–151°, λ_{max}^{EtOH} 241 mμ (ε 16,600)] and a crop of 0.4 g, mp 144–147° (yield 57%). The analytical sample (from acetone), obtained from an identical experiment, melted at 150–152°; λ_{max}^{EtOH} 241 mμ (ε 17,400).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.3; H, 9.2.

dl-**1,2,3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aα-Tetradecahydrophenanthrene-2β,7β-diol 7-Acetate** (**12**).—A solution of 6.95 g (0.031 mole) of hydroxy ketone **10** in 250 ml of tetrahydrofuran and 250 ml of ether was treated with 20 ml of dihydropyran and 200 mg of *p*-toluenesulfonic acid and the solution was left at room temperature overnight. Solid Na_2CO_3 was added to neutralize the acid and the solution was passed through a filter. Pyridine (2 ml) was added and the volume of the solution was reduced to about 30 ml by heating the mixture *in vacuo*. Tetrahydrofuran (30 ml) and absolute ethanol (60 ml) were added to the residue and the solution was added to 500 ml of ammonia. A total of 7 g (1 g-atom) of lithium wire was added to the stirred ammoniacal solution over a 0.75-hr period. The solution remained blue for about 1 hr after addition of the lithium. Absolute ethanol (30 ml) was added to discharge the color. The volume was reduced to one-third. Ether was added and the solution was heated under reflux conditions to remove more of the ammonia. Water was carefully added, followed by more ether. The layers were separated and the ether was washed with

(16) Beckman infrared spectrophotometer, Model 7.

(17) H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

saturated sodium chloride solution. The aqueous layers were washed with a fresh portion of ether and the combined ether layers were dried (Na_2SO_4). The solvent was removed *in vacuo* to afford crude ***dl*-1,2,3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aα-tetradecahydrophenanthrene-2β,7β-diol 2-dihydropyranyl ether (11)**.

Pyridine (30 ml) and acetic anhydride (15 ml) were added to the product. The next morning the excess reagents were removed by warming *in vacuo*. The residue was dissolved in 150 ml of methanol and 150 ml of 2 *N* hydrochloric acid. At the end of 0.75 hr, ether was added and the layers were separated. The ether was washed twice with saturated sodium chloride solution. The aqueous layers were washed with a fresh portion of ether and the combined ether layers were dried (Na_2SO_4). The solvent was removed by warming *in vacuo* and the residue was chromatographed on 250 g of silica gel. The fractions eluted with methylene dichloride–ether–pentane (1:2:2) afforded 2.63 g (32%) of **12**, mp 165–166°. The analytical sample, from ether, melted at 166.5–167°; λ_{max}^{KBr} 3.12 (s, hydroxyl), 5.80 and 8.00 μ (both vs, acetate).

Anal. Calcd for $C_{16}H_{26}O_3$: C, 71.14; H, 9.84. Found: C, 71.3; H, 9.9.

***dl*-3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aα-Dodecahydro-7β-hydroxy-2(1H)-phenanthrone (14)**.—A pyridine solution (30 ml) of acetate **12** (2.4 g, 0.01 mole) was added to 30 ml of pyridine containing 2.4 g of chromium trioxide. After standing for 24 hr at room temperature the reaction mixture was added to 500 ml of ethyl acetate and was then filtered through Supercel. The solvent was removed *in vacuo* and 150 ml of ether was added to the residue. More salts were filtered away and the ether was evaporated.

The crude ***dl*-3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aα-dodecahydro-7β-hydroxy-2(1H)-phenanthrone 7-acetate (13)** was dissolved in 80 ml of 5% methanolic potassium hydroxide containing 5% water and the solution was boiled under reflux for 0.75 hr. Part of the methanol was removed by warming *in vacuo*. Ether and saturated sodium chloride were added. The mixture was shaken, the layers were separated, and the ether was washed with saturated sodium chloride solution. The aqueous layers were washed again with a fresh portion of ether and the combined ether layers were dried (Na_2SO_4) and evaporated. Crystallization of the residue from ether afforded 1.34 g of **14**, mp 114–116°, and a second crop of 0.3 g, mp 108–113° (73%). The analytical sample, obtained from ether, melted at 116–117.5°; λ_{max}^{KBr} 5.91 μ (vs).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.98. Found: C, 75.9; H, 9.9.

Lithium–Ammonia Reduction of Hydroxy Ketone 14.—A solution of 30 mg (0.11 mmole) of hydroxy ketone **14** in 2 ml of tetrahydrofuran and 2 ml of absolute ethanol was added to 15 ml of ammonia. Lithium (100 mg, 14 mg-atoms), was added to the stirred solution. After 0.5 hr the blue color of the solution disappeared; the ammonia evaporated overnight. Water and ether were added, the mixture was shaken and the layers were separated. The ether was washed with saturated sodium chloride solution, dried (Na_2SO_4), and evaporated to leave a residue (40 mg).

The residue was chromatographed on a silica gel coated plate (Brinckmann PF_{254} silica gel, 20 × 20 cm) having a 1-mm coating. The plate was developed with ether–methanol (19:1). The major band from the plate afforded 25 mg of crude ***dl*-1,2,3,4-4aα,4bβ,5,6,7,8,8aα,9,10,10aα-tetradecahydrophenanthrene-2β,-7β-diol (15)**, mp 140–145°. Recrystallization from acetone containing hexane afforded 15 mg of **15**, mp 149–151°. This sample was shown to be identical with compound **15** prepared from **12** (see the second experiment below) by infrared spectral comparison, mixture melting point, and gas–liquid partition chromatography (glpc).

Sodium–Ammonia Reduction of Hydroxy Ketone 10.—A solution of 350 mg (1.6 mmoles) of hydroxy ketone **10** in 3 ml of tetrahydrofuan and 3 ml of absolute ethanol was added to 25 ml of liquid ammonia. Lithium wire (350 mg, 50 mg-atoms) was added and the solution was stirred for 1.5 hr. Ethanol was added to discharge the color. Water and ether were added, the layers were separated, and the ether layer was washed with saturated sodium chloride solution. The aqueous layers were washed with a fresh portion of ether. The combined ether layers were dried (Na_2SO_4) and concentrated. The residue was recrystallized once from acetone containing hexane and once from acetone to afford 250 mg (71%) of **15**, mp 149–151°. This sample was identical with the products described immediately above and below as shown by infrared spectral comparison, mixture melting point, glpc, and tlc.

Saponification of *dl*-1,2,3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aα-Tetradecahydrophenanthrene-2β,7β-diol 7-Acetate (12).—A solution containing 150 mg (0.6 mmole) of **12** in 15 ml of 5% methanolic potassium hydroxide containing 5% water was boiled under reflux for 0.5 hr. Water and ether were added, the mixture was shaken, and the layers were separated. The aqueous layer was washed with a fresh portion of ether and the combined ether layers were washed with saturated sodium chloride, dried (Na_2SO_4), and concentrated *in vacuo*. The residue crystallized from ether containing hexane and gave 90 mg (68%) of ***dl*-1,2,3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aα-tetradecahydrophenanthrene-2β,7β-diol (15)**, mp 149–152°. The analytical sample, obtained from acetone containing hexane, melted at 152.5–153.5°.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.94; H, 10.78. Found: C, 74.7; H, 10.5.

Catalytic Hydrogenation of Hydroxy Ketone 21.—A solution of 2 g of hydroxy ketone **21** (9.1 mmoles) in 250 ml of absolute alcohol was hydrogenated at a pressure of 3.86 kg/cm² at room temperature in the presence of 200 mg of 10% palladium-on-carbon catalyst. When no more hydrogen was absorbed the catalyst was filtered away and the solvent was removed by warming *in vacuo*.

Chromatography of 100 mg of the residue on a silica gel coated plate (Brinckmann PF_{254}, 20 × 20 cm) carrying a 1-mm coating resulted in the separation of two bands (development system, 2% methanol in ether). The more polar band afforded 30 mg of crude **14** which, on recrystallization from ether, melted at 114.5–115.5°. The compound was shown to be identical with compound **14** described earlier as shown by infrared spectral comparison, mixture melting point, and tlc. The less polar band afforded 25 mg of **23a** which, on recrystallization from ether containing hexane, gave a sample that melted at 104–106.5°. The compound was identified by its infrared spectrum, melting point, and tlc (see below).

***dl*-3,4,4aα,4bβ,5,6,7,8,8aβ,9,10,10aβ-Dodecahydro-7α-hydroxy-2(1H)-phenanthrone (16)**.—Using the lithium–ammonia procedure used for the reduction of compound **21**, phenanthrone **10** (5.5 g, 0.025 mole) afforded 2.7 g of **16**, mp 82–84°, and a second crop of 0.6 g, mp 81.5–83.5° (yield 60%). The analytical sample, obtained from ether containing hexane, melted at 82–83°.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.98. Found: C, 75.9; H, 9.9.

Sodium–Ammonia Reduction of *dl*-1,2,3,4,9,10-Hexahydro-7-methoxy-2-phenanthrol (7).[18]—Sodium (3.15 g, 0.137 g-atom) was dissolved in 1 l. of ammonia. A solution of 15 g (0.066 mole) of **7** in 100 ml of tetrahydrofuran and 25 ml of aniline[19] was added over a 20-min period to the stirred ammonia solution. At the end of the addition, 14 g (0.26 mole) of ammonium chloride was added portionwise during 5 min to discharge the blue color. The ammonia was evaporated and water and ether were added to the residue. The aqueous layer was separated and extracted twice with ether. The combined ether layers were washed three times with water, twice with 3 *N* hydrochloric acid, and three times with saturated sodium chloride solution, and dried (Na_2SO_4), and the solvent was removed to leave an amber-colored residue. After crystallization and several recrystallizations from ether containing hexane, 4.7 g of ***dl*-1,2,3,4,4aα,9,10,10aβ-octahydro-7-methoxy-2α-phenanthrol (17)**, mp 98–99°, was obtained. In a similar fashion, 168 g of **7** was reduced to yield 66.6 g of **17**, mp 97–99°, and another crop (8.8 g), mp 95–97°.

The combined mother liquors were chromatographed on 5 kg of silica gel. Fractions were combined on the basis of tlc analysis. Preliminary elution with ether–pentane (1:1) separated some less polar oils which were discarded. Continued elution with ether–pentane (1.1:1) afforded 15 g of crude ***dl*-1,2,3,4,4aα,9,-10,10aβ-octahydro-7-methoxy-2β-phenanthrol (18)**. Continued elution with the same solvent system next afforded 12 g of crude ***dl*-1,2,3,4,4aα,9,10,10aα-octahydro-7-methoxy-2β-phenanthrol (8)**. Further elution with ether–pentane (1.5:1) finally gave 53 g of an oil which yielded 13 g more of ***dl*-1,2,3,4,4aα,9,10,10aβ-octahydro-7-methoxy-2α-phenanthrol (17)**, mp 98–100° (yield, 51%). Tlc analysis showed a single spot (silica gel; developing solvent, ether; R_f 0.31). The analytical sample, obtained from

(18) This experiment was done by Mr. W. F. Wetterau.

(19) G. H. Dougles, J. M. H. Graves, D. Hartley, G. A. Hughes, B. J. McLaughlin, J. Siddall, and H. Smith, *J. Chem. Soc.*, 5072 (1963).

an earlier, less successful experiment in which aniline was not used, melted at 100–101° (from ether); infrared absorption (KBr) 9.68 and 9.55 μ; ($CHCl_3$) 9.72 μ and (CCl_4) 2.74 μ[16] (3625 cm^{-1} with band width $\approx$20 cm^{-1}).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.57; H, 8.68. Found: C, 77.4; H, 8.7.

Recrystallization of the crude *dl*-**1,2,3,4,4aα,9,10,10aβ-octahydro-7-methoxy-2β-phenanthrol** (**18**) from ether afforded 13.75 g of this *trans* product, mp 114–116° (7.5%). Tlc analysis showed a single spot (silica gel; developing solvent, ether; R_f 0.43). The analytical sample, obtained from ether, had mp 117–118°; infrared absorption (KBr) 9.61 and 10.06 μ, ($CHCl_3$) 10.10 μ and (CCl_4) 2.75 μ[16] (3631 cm^{-1} with half band width $\approx$14 cm^{-1}).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.57; H, 8.67. Found: C, 77.5; H, 8.5.

Recrystallization of the crude *dl*-**1,2,3,4,4aα,9,10,10aα-octahydro-7-methoxy-2β-phenanthrol** (**8**) from ether afforded 7 g of **6** (3.8%) identical (melting point, tlc, infrared spectrum) with an authentic sample obtained from catalytic hydrogenation of **5**.

A similar experiment afforded *dl*-**1,2,3,4,9,10-hexahydro-7-hydroxy-2-phenanthrol** (**19**), mp 196.5–198° (10%), when 100% ether was put through the column.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.72; H, 7.46. Found: C, 77.8; H, 7.6.

dl-**3,4,4aα,9,10,10aβ-Hexahydro-7-methoxy-2(1H)-phenanthrone** (**20**).[8]—A solution of 25 g (0.11 mole) of hydroxy compound **17** in 500 ml of pyridine was added to a suspension of 25 g of chromium trioxide (0.25 mole) in 500 ml of pyridine. After sitting at room temperature for 68 hr the reaction mixture was added to 1.5 l. of ethyl acetate. The chromium salts were separated by passing the suspension through Supercel. The solvent was removed by heating *in vacuo*. Ether was added to the viscous residue and the mixture was filtered again. Evaporation of the ether affored 20 g of viscous oil. Crystallization from cyclohexane containing ether afforded 6 g of **20**, mp 62–63°. Concentration of the mother liquor afforded another 4 g, mp 59–62°. Chromatography of the mother liquors on silica gel and elution with ether–pentane (1:3) afforded 6.14 g, mp 62–63° (yield 63%). The analytical sample, obtained from ether–hexane in a similar experiment, melted at 64.5–66°.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.22; H, 7.88. Found: C, 78.2; H, 7.9.

dl-**1,2,3,4,4aα,9,10,10aβ-Octahydro-7-methoxy-2α-phenanthrol** (**17**) **from** *dl*-**1,2,3,4,4aα,9,10,10aβ-Octahydro-7-methoxy-2β-phenanthrol** (**18**).—A solution of 240 mg (1.9 mmoles) of **18** in 2.5 ml of pyridine was added to 2.5 ml of pyridine containing 240 mg of chromium trioxide. After sitting at room temperature overnight the reaction mixture was added to 100 ml of ethyl acetate. The suspension was filtered through Supercel. The solvent was removed by warming *in vacuo*. Ether (50 ml) was added and more solid was filtered away. The solvent was removed leaving a residue which was dissolved in 20 ml of 95% ethanol. Sodium borohydride (240 mg, 6.3 mmoles) in 5 ml of water was added. After 20 min, acetone was added to decompose the excess borohydride. Ether and water were added, the mixture was shaken, and the layers were separated. The ether was washed with saturated sodium chloride solution. The aqueous layers were washed again with a portion of fresh ether. The combined ether solutions were dried (Na_2SO_4) and concentrated to leave an oily residue. Tlc analysis of the residue (silica gel; developing solvent, ether) showed a more polar, major component corresponding in R_f to *dl*-**1,2,3,4,4aα,9,10,10aβ-octahydro-7-methoxy-2α-phenanthrol** (**17**) and a minor component corresponding in R_f to the starting compound **18** (ratio approximately 7:3). Crystallization of the residue from ether and two recrystallizations from ether containing hexane afforded 70 mg of **17**, mp 97–99°, which was identified by melting point, mixture melting point, and infrared spectrum.

dl-**4,4aα,4bβ,5,6,7,8,8aα,9,10-Decahydro-7β-hydroxy-2(3H)-phenanthrone** (**21**).—A solution of 18.33 g (0.08 mole) of phenanthrol **17** in 186 ml of tetrahydrofuran was added to 300 ml of ammonia. Lithium wire (5.5 g, 0.8 g-atom) was added in 30 min with stirring. After 25 min a mixture of 60 ml of absolute ethanol and 60 ml of ether (anhydrous) was added to discharge the blue color. The solution was evaporated to half the volume. Ether and water were added, the mixture was shaken, and the layers were separated. The ether was washed with saturated sodium chloride solution and the aqueous layers were washed with a fresh portion of ether. The combined ether layers were dried (Na_2SO_4) and the ether was removed by warming *in vacuo*. The residue remaining was dissolved in 300 ml of dioxane and 150 ml of 2 *N* hydrochloric acid. The solution was heated in a nitrogen atmosphere for 0.5 hr on a steam bath. Saturated sodium chloride solution and ether were added to the cooled reaction mixture and the layers were separated. The ether was washed twice with saturated sodium chloride solution. The aqueous layers were washed with a fresh portion of ether. The combined ether was dried (Na_2SO_4) and the solvent was removed by warming *in vacuo*, leaving 18 g of an oily residue that crystallized from ether. Several recrystallizations from ether afforded 9.82 g of **21**: mp 138.5–140°; λ_{max}^{EtOH} 240 mμ (ϵ 16,600). Concentration of the mother liquor afforded another 0.81 g: mp 137–139°, λ_{max}^{EtOH} 240 mμ (ϵ 16,300) (yield 61%). The analytical sample, obtained from acetone in a similar experiment, melted at 141–143°.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.1; H, 9.0.

dl-**4,4aα,4bβ,5,6,7,8,8aα,9,10-Decahydro-7α-hydroxy-2(3H)-phenanthrone** (**22**).—Phenanthrol **18** (5.5 g, 0.024 mole), by a procedure identical with the one described above, afforded 2.8 g of **22** (from acetone), mp 126.5–128.5, λ_{max}^{EtOH} 241 mμ (ϵ 17,200), and a second crop of 0.6 g, mp 123.5–127° (yield 64%).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.6; H, 9.0.

Lithium–Ammonia Reduction of *dl*-**4,4aα,4bβ,5,6,7,8,8aα,9,10-Decahydro-7β-hydroxy-2(3H)-phenanthrone** (**21**).—A solution of 10.75 g (0.049 mole) of **21** in 225 ml of tetrahydrofuran and 110 ml of ether was added in a steady stream to a stirred solution of ammonia (1.1 l.) containing 1.37 g (0.19 g-atom) of lithium wire. The dropping funnel used for the addition was rinsed with another 55 ml of tetrahydrofuran. Ammonium chloride (10 g, 0.19 mole) was added as quickly as possible with controlled boiling. The solvent was evaporated to half the volume. Water (300 ml) and ether (300 ml) were added. The ether was boiled under reflux to remove more of the ammonia. More ether and water were added and the layers were separated. The ether layer was washed with saturated sodium chloride and was then dried (Na_2SO_4). Evaporation of the ether left an oily residue of 11.6 g. The residue was chromatographed on 300 g of silica gel. Elution with methylene dichloride–ether–pentane (2:5:3) afforded 7.9 g of *dl*-**3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-dodecahydro-7β-hydroxy-2(1H)-phenanthrone** (**23a**), mp 107–109° (73%). The analytical sample (from acetone), obtained from an identical experiment, melted at 107–108°.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.98. Found: C, 75.9; H, 9.9.

Further elution of the column with ether–methanol (19:1) afforded 0.9 g of *dl*-**1,2,3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-tetradecahydrophenanthrene-2α,7β-diol** (**23b**), mp 214–216° (8%). The analytical sample, from ether, melted at 216–218°.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.96; H, 10.88. Found: C, 74.9; H, 10.9.

dl-**3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-Dodecahydro-7α-hydroxy-2(1H)-phenanthrone** (**23e**).—Using the reduction procedure described in the preceding experiment, phenanthrone **22** (3.2 g, 0.014 mole) afforded 1.49 g of **23e**, mp 137.5–139°, and a second crop of 0.16 g, mp 134–137° (yield 50%). The analytical sample, obtained from ether, melted at 137.5–138°.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.98. Found: C, 75.9; H, 9.7.

dl-**3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-Dodecahydro-7β-hydroxy-2(1H)-phenanthrone Amidinohydrazone Hydrochloride** (**23c**).—A solution of 3.5 g (0.016 mole) of hydroxy ketone **23a** in 50 ml of methanol was added to 115 ml of methanol containing 4.93 g (0.036 mole) of aminoguanidine bicarbonate and 12 ml of concentrated hydrochloric acid. After sitting at room temperature overnight, the reaction mixture was added to 1 l. of ether. A precipitate formed which was found to be crude aminoguanidine hydrochloride. Dilution of the filtrate with more ether then precipitated the crude product **23c** (3.28 g, 66%): mp 250–253°, λ_{max}^{EtOH} 229 mμ (ϵ 17,200). Recrystallization was effected by adding ether to a methanolic solution of the solid. The analytical sample, from the same solvent, melted at 245–253° (evacuated tube); λ_{max}^{EtOH} 228 mμ (ϵ 18,200).

Anal. Calcd for $C_{15}H_{26}N_4O \cdot HCl$: C, 57.29; H, 8.64; N, 17.79. Found: C, 57.3; H, 8.6; N, 17.5.

dl-**3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-Dodecahydro-7β-hydroxy-2(1H)-phenanthrone 2,2-Ethylene Dithioketal** (**23d**).—A solution of 4 g (0.018 mole) of hydroxy ketone **23a** in 50 ml of glacial

acetic acid was treated with 5 ml of ethanedithiol. The mixture warmed slightly to effect solution and 4 ml of boron trifluoride etherate was added to the warm solution. After the mixture had stood at room temperature for 5 min, water was added and the precipitated solid was collected. The solid (4.5 g) was dissolved in 100 ml of 5% methanolic potassium hydroxide containing 5% water and the mixture was boiled under reflux for 0.5 hr. The volume of methanol was reduced by warming *in vacuo* and ice water was added.

The precipitate was recrystallized from acetone to afford 2.94 g (56%) of **23d**, mp 128–130°. The analytical sample, from acetone, melted at 129–130°.

Anal. Calcd for $C_{16}H_{26}OS_2$: C, 64.39; H, 8.77; S, 21.47. Found: C, 64.5; H, 8.9; S, 21.6.

***dl*-1,3,4,4aα,4bβ,5,6,8,8aα,10,10aβ-Dodecahydrophenanthrene-2,7-dione (24a).**—A solution of 3.2 g (0.014 mole) of diol **23b** in 60 ml of pyridine was added to 60 ml of pyridine containing 6.4 g of chromium trioxide. After being stirred overnight the reaction mixture was added to 600 ml of ethyl acetate. The mixture was filtered through Supercel and the solvent was removed by warming *in vacuo*. Ether (150 ml) was added and more solid was removed by filtration. Upon concentration of the ether, 1.51 g of **24a**, mp 152.5–154°, precipitated. Upon further concentration, another 0.7 g, mp 149.5–151.5°, was obtained (yield 70%). The analytical sample, obtained from ether, melted at 152.5–154°.

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.7; H, 9.2.

***dl*-1,3,4,4aα,4bβ,5,6,8,8aα,9,10,10aβ-Dodecahydrophenanthrene-2,7-dione Bisamidinohydrazone Hydrochloride (24b).**—A solution of 4.83 g (0.022 mole) of diketone **24a** in 75 ml of methanol was added to a solution of 13.6 g (0.100 mole) of aminoguanidine bicarbonate and 35 ml of concentrated hydrochloric acid in 315 ml of methanol. After 24 hr at room temperature, the mixture was filtered to give 6.46 g (73%) of **24b**, mp 350° dec.

The analytical sample, obtained by adding ether to a methanolic solution of **24b**, had mp 348° dec; λ_{max}^{EtOH} 230 mμ (ε 37,800).

Anal. Calcd for $C_{16}H_{28}N_8 \cdot 2HCl$: C, 47.41; H, 7.46; N, 27.65. Found: C, 47.6; H, 7.3; N, 27.7.

***dl*-3,4,4aα,4bβ,5,6,7,8,8aα,9,10,10aβ-Dodecahydro-7,7-ethylenedimercapto-2(1H)-phenanthrene (24c).**—A solution of 2.83 g (9.4 mmoles) of thioketal **23d** in 40 ml of pyridine was added to 40 ml of pyridine containing 3 g of chromium trioxide. After 5 days at room temperature the reaction mixture was added to 500 ml of ethyl acetate. The mixture was filtered through Supercel and the filtrate was concentrated to a residue by warming *in vacuo*. Ether (200 ml) was added to the residue and more unwanted solid was separated. The ether was concentrated and 2 g of **24c**, mp 132–133°, was obtained. Another 150 mg, mp 131–132°, was obtained from the mother liquor (yield 76%).

Anal. Calcd for $C_{16}H_{24}OS_2$: C, 64.82; H, 8.16; S, 21.62. Found: C, 64.8; H, 8.1; S, 20.9.

***dl*-3,4,4aα,4bβ,5,6,8,8aα,9,10-Decahydrophenanthrene-2,7-dione (25).**—A solution of 5.14 g (0.023 mole) of hydroxyphenanthrone **21** in 50 ml of pyridine was added to 50 ml of pyridine containing 5.15 g of chromium trioxide. After being stirred overnight the reaction mixture was added to 500 ml of ethyl acetate. The mixture was passed through Supercel and the solvent was then removed by warming *in vacuo*. Ether (150 ml) was added and more solid was filtered away. The solvent was evaporated leaving 4.69 g of an oily residue that crystallized. Recrystallization from ether afforded 3.27 g (63%) of **25**, mp 123–125°. The analytical sample, obtained from ether, melted at 124–125°; λ_{max}^{EtOH} 238 mμ (ε 16,600).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.02; H, 8.30. Found: C, 77.1; H, 8.5.

Lithium–Ammonia Reduction of *dl*-4,4aα,4b,5,6,7,8,8aα,9,10-Decahydro-7β-hydroxy-4bβ-methyl-2(3H)-phenanthrone (26).[14]—Using the procedure described for the reduction of **21**, 2.04 g (8.65 mmoles) of phenanthrone **26** afforded 0.99 g of ***dl*-3,4,4aα,-4b,5,6,7,8,8aα,9,10,10aβ-dodecahydro-7β-hydroxy-4bβ-methyl-2-(1H)-phenanthrone (27)**, mp 105–107° (from ethyl acetate), and a second crop of 0.1 g, mp 103–105° (54%).

Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.2; H, 10.1.

***dl*-1,2,3,4,4aα,4b,5,6,7,8,8aα,9,10,10aβ-Tetradecahydro-4bβ-methylphenanthrene-2α,7β-diol (28**, 0.19 g, mp 171–175°) was also isolated (9%) from the same reaction. Recrystallization from acetonitrile afforded a sample that melted at 182–184°.

Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.83; H, 10.84.

***dl*-3,4,4aα,4b,5,6,7,8,8aα,9,10,10aβ-Dodecahydro-7β-hydroxy-1β,4bβ-dimethyl-2(1H)-phenanthrone (29).**—Dry liquid ammonia was prepared by treatment of 300 ml of liquid ammonia with lithium wire until the blue color presisted, followed by distillation until 100 ml of liquid ammonia had been condensed in the reaction vessel. To the dry liquid ammonia was added with stirring 0.16 g (23 mg-atoms) of lithium wire followed by dropwise addition of a solution of 1.00 g (4.23 mmoles) of **26** in 15 ml of tetrahydrofuran and 35 ml of anhydrous ether over a 10-min period. The mixture was stirred for 30 min and then treated with 1.2 ml of methyl iodide which immediately discharged the blue color. The ammonia was allowed to evaporate and the residue was treated with 100 ml of water and extracted with 250 ml of ether. The extract was washed with water and saturated salt solution and dried ($MgSO_4$). The residue (1.05 g), obtained upon evaporation of the solvent, was chromatographed on 30 g of silica gel. Elution with 1:1:3 methylene dichloride–ether–pentane afforded crystalline material which, upon recrystallization from acetonitrile, furnished 0.34 g of crude **29**, mp 115–120°. One recrystallization of a 0.19-g portion from the same solvent gave 0.125 g of **29**, mp 123–127°. The analytical sample, which was prepared by recrystallization from the same solvent, melted at 129–132°.

Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.5; H, 10.3.

Crystalline 6-Methoxy-1-methyl-2-tetralone (30).—A sample of compound **30**,[20] bp 110–112° (0.1 mm), crystallized upon cooling in a refrigerator. Two recrystallizations from ether afforded a sample: mp 45.5–47°; λ_{max}^{EtOH} 224 mμ (ε 7000), 278 (2050), and 282 (1850).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.7; H, 7.7.

Registry No.—**4,** 10232-41-4; **5,** 10232-44-7; **6,** 10232-45-8; **7,** 10232-46-9; **8,** 10232-47-0; **9,** 10232-48-1; **10,** 10232-49-2; **12,** 10232-50-5; **14,** 10232-51-6; **15,** 10232-52-7; **16,** 10232-53-8; **17,** 10232-54-9; **18,** 10232-55-0; **19,** 10232-56-1; **20,** 10232-57-2; **21,** 10232-58-3; **22,** 10232-59-4; **23a,** 10232-60-7; **23b,** 10232-61-8; **23c,** 10232-62-9; **23d,** 10232-42-5; **23e,** 10232-63-0; **24a,** 10232-64-1; **24b,** 10232-65-2; **24c,** 10232-43-6; **25,** 10232-66-3; **27,** 10232-67-4; **28,** 10232-68-5; **29,** 10232-69-6; **30,** 5111-67-1.

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