# The Acid-Catalyzed Cyclization of 2,3-Dimethyl-2-phenethyl-3-cyclohexen-1-one

Takenori KUSUMI, Nobuo OHNO, and Hiroshi KAKISAWA

*Department of Chemistry, Tokyo Kyoiku University, Otsuka, Bunkyo-ku, Tokyo 112*

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The cyclization of 2,3-dimethyl-2-phenethyl-3-cyclohexen-1-one **6a** with aluminum chloride gave 4a,*cis*-10a-dimethyl-3,4,4a,9,10,10a-hexahydro-1(2*H*)-phenanthrone **8a**. The stereochemistry of the latter was established by synthesizing 4a,*cis*-10a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **10** through Diels-Alder reaction of 3-formyl-4a,*cis*-8a-dimethyl-4a,5,6,7,8,8a-hexahydro-2(1*H*)-naphthalenone **20** with butadiene.

The acid-catalyzed cyclization of aryl-olefin systems is widely used in the synthesis of steroids and polycyclic terpenes. Two asymmetric centers are produced at the ring junctions of the newly constructed ring. Recently the stereochemical investigation of this 'cyclialkylation' is reported by Ireland *et al.*[1] In their and hitherto reported cyclialkylation reactions, two newly formed angular substituents are restricted mostly to hydrogen and methyl groups, and there has been no report upon such cyclialkylation that gives rise to two angular methyl groups, which should be of importance especially in the synthetic study of triterpenes.

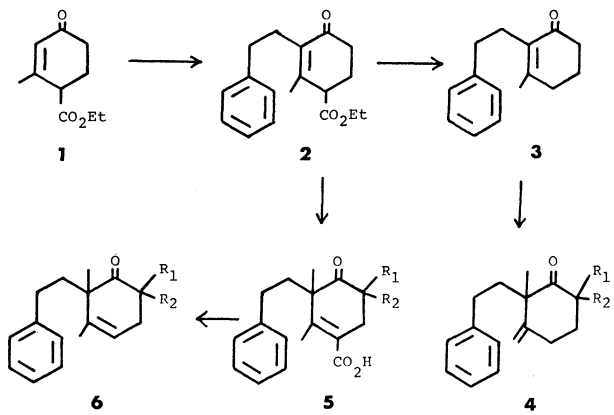
This report deals with the cyclialkylation of 2,3-dimethyl-2-phenethyl-3-cyclohexen-1-one **6a**, which affords the octahydrophenanthrene **8b** carrying two methyl groups at the angular positions.

The synthesis of 4a,*cis*-10a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **10** which serves as a standard for establishing the stereochemistry of 4a,10a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrenes is also described.

## Results and Discussion

*Synthesis and Cyclization of the Phenethylcyclohexenone 6a.* Hageman's ester **1** readily availabe by condensation of ethyl acetoacetate and paraformaldehyde[2] was treated with phenethyl bromide and sodium hydride in benzene-dimethylformamide (DMF) to give the phenethyl derivative **2**, which was boiled with potassium hydroxide in ethanol affording the cyclohexenone **3**.[3] Methylation of **3** with methyl iodide and sodium hydride (one equivalent) in benzene-DMF gave a mixture of mono, di, and trimethylated products (**4a**—**c**) accompanied by unchanged **3**. The formation of the exocyclic double bond by the methylation was revealed by the NMR spectrum (4.83 and 4.90 ppm, each br. s, 2H) of the product. The yield of the methylated product was estimated as 30% by vpc. However, it was practically difficult to separate the desired monomethylated derivative **4a** from the reaction mixture.

The yield of the methylation was raised as high as 50% when the ketoester **2**, in which the carbethoxy group at C-4 activates the enone system, was treated with methyl iodide and sodium hydride in toluene. The crude product was directly hydrolyzed with potassium hydroxide in ethanol to afford a mixture of the ketoacids **5a**—**c** easily separable from the cyclohexenone **3** which was produced from the unreacted ester **2** through the hydrolysis and decarboxylation. The mixture of the acids **5a**—**c** was treated with copper chromite catalyst in quinoline[4] to yield the decarboxylated products **6a**, **b**, and **c**. From the vapor phase chromatogram the ratio of **6a**, **b**, and **c** was estimated as 62: 28: 10.



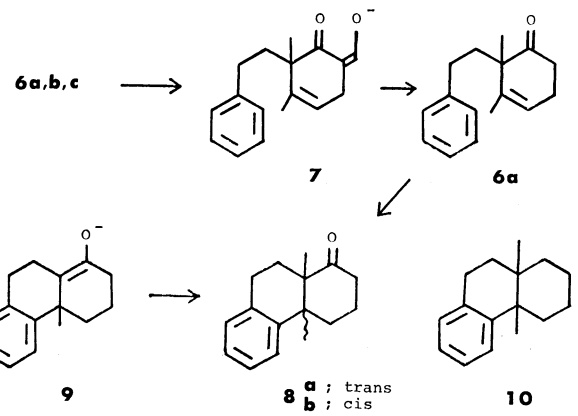

a: $R_1=R_2=H$, b: $R_1=CH_3$, $R_2=H$, c: $R_1=R_2=CH_3$

Isolation of the desired monomethylated derivative **6a** was achieved as follows; formylation of the mixture of **6a**—**c** followed by alkaline extraction gave a solution of the enolate **7** which was hydrolyzed to produce **6a**. Di and trimethylated derivatives, **6b** and **c**, could be removed in the course of the alkaline extraction.

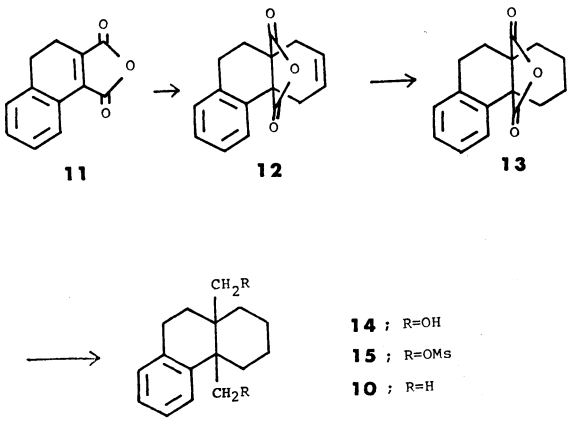
Treatment of **6a** with aluminum chloride in carbon disulfide at 0 °C gave a crystalline substance (mp 64—65 °C) as a single product in 73% yield. Treatment of **6a** with 85% phosphoric acid at 120 °C afforded the same product.

The IR spectrum of the product represents a carbonyl absorption at 1702 $cm^{-1}$ and the NMR spectrum shows two sharp singlets at 1.10 and 1.27 ppm ascribable to tertiary methyls beside a 4H-multiplet at the aromatic region. From these spectral properties the structure **8** was assigned for the crystalline product.

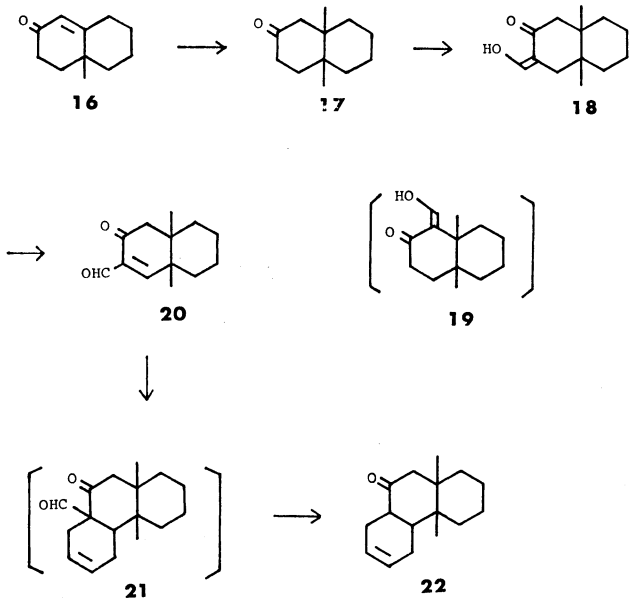
The NMR and the vpc showed that the only one of the two possible stereoisomers, **8a** and **b**, was afforded by the cyclization reaction. Whitlock and Overman have obtained *trans* **8a** and *cis* **8b** through Simmons-Smith reaction of the enolate **9**,[5] and our product **8** is revealed to accord with *cis* **8b** by comparison with its mp and the NMR spectrum. However, no basis to determine the stereochemical relationship of the two angular methyl groups is appeared in their report. Therefore we focussed our attention upon synthesizing the *cis*-dimethylhydrophenanthrene **10** by the stereochemically unambiguous method.




*Synthesis of the* cis-*Dimethylhydrophenanthrene* **10**. The anhydride **12**, prepared by Diels-Alder reaction[6] of **11** and butadiene, was hydrogenated on palladium–charcoal in ethanol affording **13**. This was treated with lithium aluminum hydride in ether to produce the diol **14**. It is obvious from surveying the series of the reaction employed that the two hydroxymethyl groups of **14** should be situated in a *cis* sence. The diol **14** was treated with methanesulfonyl chloride in pyridine at 0 °C to give the dimesylate **15**. Reduction of **15** with lithium aluminum hydride in ether or tetrahydrofuran, however, produced an intractable mixture of rearranged hydrocarbons, ethers and alcohols, and the desired *cis*-dimethyl compound **10** could not be obtained from the mixture.

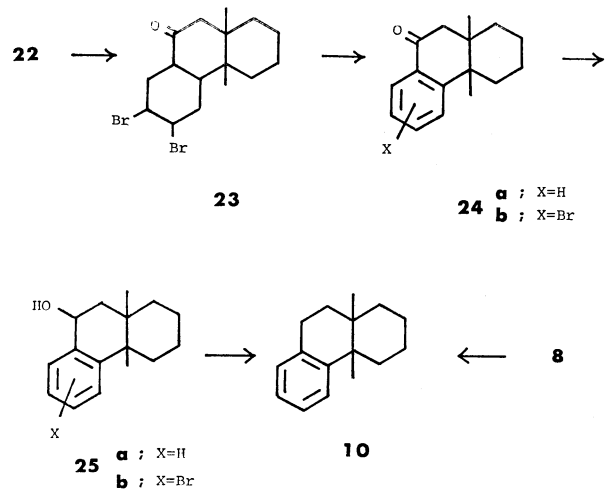



We, therefore, turned our effort to another approach to **10**. The *cis*-dimethyldecalone **17** was prepared by treatment of the octalone **16** with methylmagnesium iodide–cuprous salt[7] or dimethylcopperlithium,[8] the latter giving the higher yield. The *cis*-relationship of the two methyl groups in **17** has been already established.[7] The decalone **17** was formylated with ethyl formate and sodium methoxide to give **18** in good yield. The NMR spectrum of **18** exhibits two pairs of AB quartet centered at 2.28 (2H, $J$=15 Hz) and 2.29 (2H, $J$=19 Hz) ppm attributable to the methylene groups at C-1 and C-4, which excludes the another possible isomer **19**. The regiospecific formylation at C-3 is ascribed to severe steric hindrance around C-1 of the decalone **17**. The formylketone **18** was converted into **20** by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dioxane.[9] The NMR spectrum of the ketoaldehyde **20** shows five sharp singlets at 10.06 (1H, -CHO), 7.40 (1H, olefinic proton at C-1), 2.43 (2H, $-CH_2-$ at C-4), 1.16 (3H, $-CH_3$), and 1.05 (3H, $-CH_3$) ppm. The ketoaldehyde **20** was heated with butadiene at 200 °C, and the product was chromatographed to give rise to a ketonic substance in 7% yield. The IR spectrum of this ketone shows a strong absorption at 1710 (C=O) and a weak one at 1665 $cm^{-1}$ (C=C). Its NMR spectrum exhibits two sharp singlets at 1.04 (3H) and 1.06 (3H) assignable to two quarternary methyls and a broad singlet at 5.60 (2H) ppm due to two olefinic protons. No signal showing the presence of an aldehyde proton was observed. From these spectral properties the structure **22** could be assigned for the ketone, and this was further justified by its mass spectrum. The molecular peak appears at *m/e* 232.184 accordant with the molecular weight of **22** (232.183 Calcd for $C_{16}H_{24}O$). Carbon monoxide was apparently removed from the initial Diels-Alder adduct **21** in the course of the reaction.




The tricyclic ketone **22** was converted into the dibromide **23** through the agency of bromine in chloroform. Dehydrobromination of **23** with quinoline[10] and subsequent dehydrogenation with DDQ gave a mixture of **24a** and **b**. The mixture was treated with lithium aluminum hydride affording **25a** and **b**. Reduction of the mixture with sodium in liquid ammonia in the presence of ethanol[11] and purification with column chromatography gave rise to the *cis*-dimethylhydrophenanthrene **10** as an oil. Its NMR spectrum exhibits two sharp singlets at 0.95 and 1.19 due to the angular methyl groups, a broad triplet at 2.84 (2H, $J$=7 Hz) ppm corresponding to the benzylic protons and a complex multiplet in the aromatic region (4H, 7—7.7 ppm). The IR and the mass spectra are also consistent with the structure **10**.

Finally the tricyclic ketone **8**, which had been obtained by the cyclization of **6a**, was reduced by hydrazine and sodium hydroxide to produce a hydrocarbon. The IR spectrum and the behavior on tlc and vpc of the hydrocarbon were identical with those of **10**. These facts show that the two angular methyl groups of **8**




are in a *cis*-relationship.

The acid-catalyzed cyclization of **6a** proceeds in such a manner as to yield *cis* **8b** exclusively.

## Experimental

NMR spectra were obtained with a Hitachi EPI-S2 spectrophotometer. Ultraviolet spectra were taken on a Hitachi EPS-3T. Melting points and boiling points are uncorrected.

*3-Methyl-2-phenethyl-2-cyclohexen-1-one* **3** was prepared according to the method described in Ref. 3.

*Methylation of 3-Methyl-2-phenethyl-2-cyclohexen-1-one* **3**. Into a suspension of sodium hydride (270 mg as a 50% dispersion in mineral oil) in dry benzene (30 ml) and DMF (10 ml) was added a solution of **3** (1.0 g) in benzene (5 ml) during 1 hr in an atmosphere of nitrogen. After the mixture was stirred at room temperature for 20 hr, a solution of methyl iodide (730 mg) in benzene (5 ml) was added during 1.5 hr. After being stirre at 40—45 °C for 18 hr, the mixture was washed with dilute hydrochloric acid, sodium bicarbonate solution and dried over sodium sulfate. Evaporation of the solvent gave an oil (1.1 g), which consisted of the starting ketone **3** and the methylated products **4a—c**. The ketone **3** could be removed by preparative thin layer chromatography, but the methylated products showed the single spot on tlc and approximate retention times on vpc, and the further attempt to isolate **4a** was discontinued. The mixture of **4a—c** has the following spectral properties; $\nu$(film) 1705, 1630, 1600, 895, 750, 700 $cm^{-1}$; $\delta$ ($CDCl_3$) 4.83 (br.s, 1H), 4.90 (br.s, 1H) ppm; *m/e* 256 ($M^+$ of **4c**), 242 ($M^+$ of **4b**), 228 ($M^+$ of **4a**).

*Methylation of* **2**.[3] A solution of **2** (28.7 g) in dry toluene (170 ml) containing sodium hydride (5.90 g) was stirred at 110 °C until no more hydrogen was evolved (1.5 hr). The cooled reaction mixture was treated with methyl iodide (71.0 g) and the mixture was stirred at refluxing temperature for 70 hr. Ethanol was added to the cooled mixture and the mixture was poured into water. The toluene layer was separated, and the aqueous layer was extracted with ether. The combined organic layer was washed with sodium bicarbonate solution and dried. The solvent was removed to afford a yellow oil (29.6 g). This was dissolved into 15% ethanolic sodium hydroxide (120 ml) and the solution was heated under reflux for 23 hr. Water was added and the mixture was further refluxed for 1 hr. The ethanol was removed and the residue was treated with water and extracted with ether. The ethereal layer was washed with sodium bicarbonate solution. The aqueous layers were combined and acidified with 1.4 M hydrochloric acid to pH 1.0. Extraction with ether and removal of the ether gave a mixture of the acids **5a—c** (15.3 g). From the ethereal layer was obtained the ketone **3** (8.9 g).

*Decarboxylation of the Acids* **5a—c**. A mixture of the acids **5a—c** (15.3 g), copper chromite catalyst[4] (1.5 g), and freshly distilled quinoline (60 ml) was heated to reflux in a metal-bath for 10 min. The cooled reaction mixture was poured into ether and the catalyst was filtered away. The filtrate was washed with dilute hydrochloric acid, sodium bicarbonate solution and brine, and dried over sodium sulfate. The crude deep brown oil obtained after removal of the ether was fractionated under reduced pressure to afford a light yellow oil (6.9 g; bp 108—123 °C/0.2 mmHg). The oil was found to consist of **6a** (62%), **6b** (28%), and **6c** (10%) by vpc (PEGS-10% on chromosorb W; 228°C).

*Isolation of* **6a** *from the Mixture* **6a—c** *by Formylation.* Into an ice-cooled suspension of powdered sodium methoxide (1.35 g) in dry benzene (30 ml) was added with stirring a solution of the above mixture **6a—c** (3.07 g) in ethyl formate (2.0 g) under a nitrogen atmosphere. The mixture was allowed to stand at room temperature overnight. Ice–water was added, and the alkaline-insoluble materials (**6b** and **c**) were taken up into ether. The aqueous alkaline solution was kept at 90 °C for 4 hr. The cooled solution was extracted with ether, dried over sodium sulfate. Removal of the ether afforded the cyclohexenone **6a** (1.18 g), $\nu$ (film): 3020, 1705, 1620, 1600, 750, 695 $cm^{-1}$; $\delta$ ($CCl_4$): 1.18 (s, 3H), 1.79 (br.d, 3H), 2.0—2.7 (m, 8H), 5.73 (m, 1H), 7.2 (br.s, 5H) ppm; *m/e* 228.150; Calcd for $C_{16}H_{20}O$: 228.150; bp 110 °C/0.1 mmHg.

*Cyclization of 2,3-Dimethyl-2-phenethyl-3-cyclohexen-1-one* **6a**. *(A) With Aluminum Chloride*: The cyclohexenone **6a** (96 mg) was stirred with anhydrous aluminum chloride (143 mg) in dry carbon disulfide (5 ml) at 0 °C for 3 hr. The mixture was filtered and the filtrate was washed with dilute hydrochloric acid. Evaporation of the solvent gave a colorless solid (70 mg; 74%). Recrystallization from benzene–hexane gave pure **8b**, mp 64—65 °C; $\nu$ (KBr): 1702, 1498, 755 $cm^{-1}$; $\nu$ ($CHCl_3$): 1700, 1603, 1498 $cm^{-1}$; $\delta$ ($CDCl_3$): 1.10 (3H, s), 1.27 (3H, s), 1.5—3.0 (m, 10H), 7.0—7.3 (4H, m) ppm; $\delta$ ($C_6H_6$): 1.00 (3H, s), 1.06 (3H, s) ppm. Found: C, 84.03; H, 8.80%. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83%.

*(B) With Phosphoric Acid*: The cyclohexenone **6a** (593 mg) was heated at 120—125 °C with 85% phosphoric acid (50 ml) for 12 hr. The cooled mixture was poured into ice–water, and extracted twice with ether. The ether was evaporated to give 650 mg of oil which was chromatographed on alumina (50 g). Elution with benzene gave **8b** (443 mg; 75%), which was identical with the ketone obtained by the method (A).

*4b,5,8,8a,9,10-Hexahydrophenanthrene-4b,8a-dicarboxylic Anhydride* was prepared according to the Ref. 6; mp 84 °C.

*4b,5,6,7,8,8a,9,10-Octahydrophenanthrene-4b,8a-dicarboxylic Anhydride* **13**. The anhydride **12** (1.7 g) was dissolved in ethyl acetate (100 ml) and platinum oxide (400 mg) was added. The mixture was stirred under hydrogen. The hydrogen absorption ceased after the uptake of 267 ml of hydrogen and the catalyst was filtered away. The filtrate was concentrated to give an oil (1.71 g) which solidified on standing. Recrystallization from benzene–ligroin gave colorless needles; mp 97—98 °C; $\nu$ (KBr): 1850, 1775 $cm^{-1}$.

*4b,8a-Bis(hydroxymethyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthrene* **14**. Into a stirred suspension of lithium aluminum hydride (2.1 g) in tetrahydrofuran (250 ml) was added a solution of the anhydride **13** (1.35 g) in tetrahydrofuran

(10 ml). The reaction mixture was heated under reflux for 17 hr. The complex was decomposed with water and the white precipitates were filtered away. The filtrate was concentrated to give a colorless solid (1.31 g). Recrystallization from ethanol afforded colorless needles (1.1 g); mp 130—132 °C; $\nu$ (KBr): 3300—3200 $cm^{-1}$.

*4b,8a-Bis(methanesulfoxymethyl)-4b,5,6,7,8,8a,9,10-octahydrophenanthrene* ***15***. The diol **14** (200 mg) was dissolved in pyridine (40 ml) and the solution was cooled at 0 °C in an ice-bath. Methanesulfonyl chloride (2.8 ml) was added in a portion, and the reaction mixture was stirred at 0 °C for 1 hr. This was poured onto ice, and the aqueous solution was extracted with ether. The ethereal solution was washed successively with 2 M hydrochloric acid, sodium bicarbonate solution, water and brine. After the ethereal solution was dried over sodium sulfate, the solvent was evaporated to yield a colorless solid (354 mg), which was washed with small portions of ether. The dimesylate has the following spectral properties; $\nu$ (KBr): 1335, 1170, 980 $cm^{-1}$; $\delta$ ($CDCl_3$): 2.85 (3H, s), 3.05 (3H, s), 4.30 (2H, s), 4.41 (2H, ABq, $J$=9 Hz), 7.2 (4H, m) ppm.

*Reduction of 15 with Lithium Aluminum Hydride.* A mixture of the dimesylate (285 mg) and lithium aluminum hydride (600 mg) in ether (100 ml) was heated under reflux with stirring overnight. After the usual treatment a colorless oil was obtained. The IR spectrum of the crude product showed strong absorption at 1170 $cm^{-1}$ suggesting the presence of ethers in the product. The oil was chromatographed on silicic acid. Elution with hexane gave a mixture of hydrocarbons (90 mg) whose NMR spectrum showed no distinct methyl signals.

*3,4,4a,5,6,7,8,8a-Octahydro-4a,*cis*-8a-dimethyl-2(1H)-naphthalenone* ***17***. Into a suspension of cuprous iodide (34.8 g) in ether (400 ml) was added methyllithium (2 eq) in ether at −20 °C under a slow stream of nitrogen. Into the dark brown solution was added a solution of **16** (20 g) in ether (50 ml) at 0 °C during 25 min. After the reaction mixture was stirred at 0 °C for 2.5 hr, aqueous ammonium chloride solution was added cautiously. After violent evolution of gas ceased, the mixture was transferred into a separatory funnel. The ethereal layer was separated and washed with brine and dried over sodium sulfate. Evaporation of the ether afforded a crystalline solid (20.4 g) which was purified by chromatography (1 kg of alumina). Elution with hexane–benzene (8:2) yielded **17** (17.7 g; 80%). Further purification by sublimation (50 °C/1 mmHg) gave colorless crystals; mp 119—127 °C (lit, 109—116 °C). The IR and NMR spectra were identical with those of **17** prepared by Marshall's method.[7]

*3-Formyl-4a,*cis*-8a-dimethyl-3,4,4a,5,6,7,8,8a-octahydro-2(1H)-naphthalenone* ***18***. Sodium methoxide prepared by dissolving sodium (186 mg) in dry methanol (3 ml) was heated at 160 °C at 1 mmHg for several minutes to remove the trace of methanol. The solid was dispersed into dry benzene (20 ml) and a solution of the decalone **17** (300 mg) in freshly distilled dry ethyl formate (670 mg) was added at 0 °C during 15 min. After the temperature was maintained at 0 °C for 1 hr, the mixture was stirred at room temperature overnight. The yellow slurry was treated with ice-water and the aqueous layer was separated and washed with ether. The alkaline solution was acidified with hydrochloric acid, and the acidic material was extracted with ether. The usual treatment of the ether extract gave a slightly red oil (349 mg) which was used in the next reaction without further purification; $\nu$ (film): 1645, 1595 $cm^{-1}$; $\delta$ ($CDCl_3$): 0.98 (s, 6H), 2.28 (ABq, $J$=15 Hz, 2H), 2.29 (ABq, $J$=19 Hz, 2H) ppm.

*3-Formyl-4a,*cis*-8a-dimethyl-4a,5,6,7,8,8a-hexahydro-2(1H)-naphthalenone* ***20***. A solution of the formylketone **18** (5.6 g) and DDQ (6.2 g) in dry dioxane (60 ml) was allowed to stand at room temperature for 30 min. Fine precipitates separated out rapidly. The precipitates were filtered off, and the filtrate was diluted with methylene chloride. The solution was washed with 2% aqueous sodium hydroxide solution until the aqueous layer showed no coloration. The organic layer was washed with water and brine, and dried over sodium sulfate. Evaporation of the solvent gave a red oil (3.2 g) which was purified by distillation at reduced pressure, bp 109 °C/0.2 mmHg (2.6 g). The oil solidified on cooling and recrystallization from hexane afforded light yellow crystals; mp 35—36 °C; $\nu$ ($CCl_4$): 1705, 1690, 1615 $cm^{-1}$; $\delta$ ($CCl_4$): 1.05, 1.16 (each 3H, s), 2.43 (2H, s), 7.40 (1H, s), 10.06 (1H, s) ppm. Found: C, 75.65; H, 8.77%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%.

*4b,*cis*-8a-Dimethyl-1,4,4a,5,6,6a,7,8,9,10,10a-dodecahydro-10-oxophenanthrene* ***22***. The ketoaldehyde **20** (1.6 g) and butadiene (1.26 g; 3 eq) in dry dioxane (5 ml) was heated at 200—210 °C for 24 hr in a sealed tube. The resulting oil was chromatographed on silicic acid (100 g), and elution with hexane–benzene (3:7) yielded the ketone **22** (107 mg). The analytical sample was obtained by micro distillation of a small portion of this material at 120—140 °C bath temperature (0.4 mmHg). Found: *m/e* 232.184. Calcd for $C_{16}H_{24}O$: 232.183.

*2,3-Dibromo-4b,*cis*-8a-dimethyl-1,2,3,4,4a,4b,5,6,7,8,8a,9,10,10a-tetradecahydro-10-oxophenathrene* ***23***. Into a stirred solution of the tricyclic ketone **22** (111 mg) in freshly distilled chloroform was added a solution of bromine (92 mg) in dry carbon tetrachloride (4 ml) at −60 °C during 40 min. The mixture was stirred at −60 °C for 10 min, and the solvent was evaporated under reduced pressure to yield a yellow oil (211 mg) which crystallized on cooling.

*Dehydrobromination of the Dibromide* ***23***. A solution of the dibromide **23** (211 mg) in freshly distilled quinoline (2 ml) was heated at 160—170 °C for 4 hr. The reaction mixture became dark brown. This was cooled and poured into water, and the product was extracted with ether. The ethereal layer was washed several times with 1 M hydrochloric acid, sodium bicarbonate solution, and dried over sodium sulfate. Removal of the solvent gave a brown oil (123 mg); $\nu$ (film): 1705, 1668, 1615, 1600 $cm^{-1}$. The crude product was treated with DDQ (192 mg) in dry benzene (10 ml) at 80 °C for 1 hr. The dark brown mixture was filtered through alumina (15 g). The alumina was further eluted with benzene (200 ml). Evaporation of the benzene gave a yellow oil (106 mg). The oil was adsorbed on silicic acid (20 g) and eluted with hexane–benzene to afford mainly three fractions (a), (b), and (c). Fraction (a) (31 mg); the starting dibromide **23**: fraction (b) (22 mg); the bromoketone **24b**, $\nu$ (film): 1705 $cm^{-1}$: fraction (c) (38 mg): a mixture of **24a** and **b**, *m/e* 306 and 308 ($M^+$ of **24b**), 228 ($M^+$ of **24a**).

*4b,*cis*-8a-Dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthrene* ***10***. A mixture of the ketones (fraction (c); 34 mg) was dissolved in ether (5 ml) and lithium aluminum hydride (359 mg) was added. The mixture was stirred at room temperature overnight. After decomposition of the excess hydride a colorless oil was obtained (32 mg); $\nu$ (film): 3400 $cm^{-1}$. Into liquid ammonia (10 ml) was added a solution of the above oil in dry ethanol (0.5 ml). Sodium (80 mg) was added in small portions. The ammonia was evaporated and the residue was treated with water. The product was extracted with ether and purified by column chromatography to give a colorless oil (20 mg); $\nu$ (film): 2900, 1480, 1460, 1438, 1375, 1034, 751, 737, 718 $cm^{-1}$; $\delta$ ($CCl_4$): 0.95 (3H, s), 1.19 (3H, s),

2.84 (2H, t, $J$=7 Hz), 7—7.7 (4H, m) ppm; *m/e* 214.169; Calcd for $C_{16}H_{22}$: 214.172.

*By Wolff-Kishner Reduction of* ***8b***. A mixture of **8b** (46 mg), 80% hydrazine hydrate (0.5 ml) and potassium hydroxide (680 mg) in diethylene glycol (5 ml) was refluxed for 1 hr. Water was then distilled until the temperature of the reaction mixture reached 200 °C, and the distillate was collected. The reaction mixture was kept at 200 °C for 3 hr. Water was added and the mixture was acidified with conc. hydrochloric acid. The mixture and the distillate were combined and extracted with benzene. After drying over sodium sulfate, the benzene was removed on a rotary evaporator to give a colorless oil (30 mg) which was purified with chromatography (silicic acid; 2 g). Elution with hexane afforded a colorless oil (20 mg). The IR spectrum, $R_f$ value on tlc, and retention time on vpc were identical with those of **10** obtained in the above procedure.

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