Stereochemical Studies of Octahydrophenanthrenes. I[1]

ZOLTAN G. HAJOS, KARL J. DOEBEL, AND M. W. GOLDBERG[2]

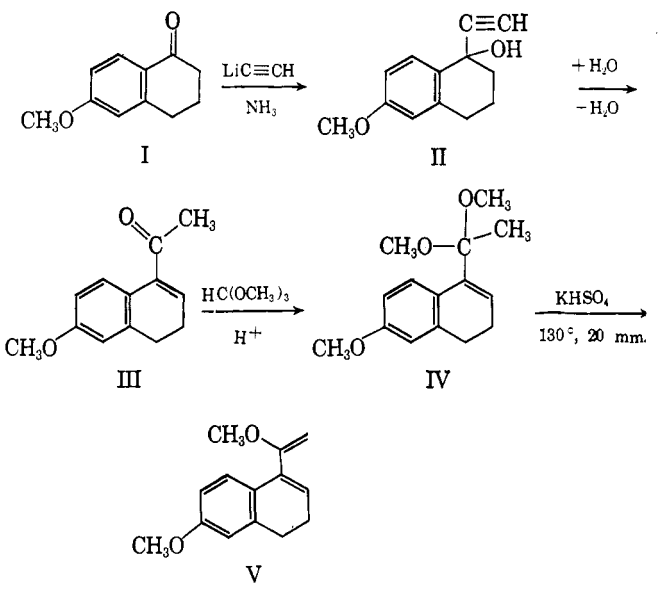
Department of Chemical Research, Research Division, Hoffmann-La Roche, Inc., Nutley, New Jersey

Received January 29, 1964

Three stereoisomeric 7-methoxy-4-oxooctahydro-1-phenanthrenecarboxylic acids (XV, XI, and XIII) were obtained from the addition products of methyl acrylate and the diene V. The stereochemistry of these acids (two *cis* and one *trans* structure) was established by conversion into the corresponding desoxo acids XXIII, XXIV, and XXII, two of which, the *cis-syn* and the *cis-anti* desoxo acids XXIII and XXIV, were found to be identical with the acids obtained by sodium hypobromite oxidation of the corresponding methyl ketones (XXVI and XXVII). The latter were prepared by catalytic hydrogenation of 1-acetyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XXV). The third desoxo acid (XXII) represents the *trans* structure. Nuclear magnetic resonance spectroscopy provided additional proof for the stereochemistry of the three stereoisomeric keto acids XV, XI, and XIII.

The present investigation was undertaken as part of a broader program aimed at the synthesis of steroid-like compounds. It involved the Diels–Alder addition of methyl acrylate to the diene V, 1-(1′-methoxyvinyl)-3,4-dihydro-6-methoxynaphthalene, and led to several new octahydrophenanthrene-1-carboxylic acids, with oxygen functions on C-4 and C-7. The diene V was obtained from 6-methoxy-1-tetralone (I) as shown in Chart I.

CHART I



Reaction of the tetralone I with lithium acetylide in liquid ammonia yielded the known acetylenic carbinol II.[3] This was converted into the unsaturated methyl ketone III, in refluxing methanol–water with a mercurated cation-exchange resin,[4] to catalyze the simultaneous hydration and dehydration reactions. Treatment with trimethyl orthoformate and acid converted the ketone III into the dimethyl ketal IV, which upon heating with $KHSO_4$ at 130° *in vacuo* yielded the diene V with the loss of 1 mole of methanol.

The Diels–Alder reaction of diene V with methyl acrylate gave a mixture of addition products, distilling at 174–176° under high vacuum. The ultraviolet spectrum of this mixture had a maximum at 265 mμ (ε 18,200), which is in accordance with previous findings on similar compounds.[5] Literature data[6a–c] indicated that the polarity of the diene should affect the ratio of the structural isomers formed in a Diels–Alder reaction with an unsymmetrical dienophile, and, since it can be assumed that the C-1′ methoxy group in diene V increases the electron density at C-2′ in the vinyl side chain, it was to be expected that in the reaction with methyl acrylate 1-substituted addition products should predominate.

Inspection of the two transition states for a C-1 and C-2 addition, on the other hand, would predict a less unidirectional addition.[6d–f]

Vapor phase chromatography of the mixture of adducts showed the presence of three components: the 1β-ester (VI) in about 80%, the 1α-ester (VII) in about 18%, and a third product, most probably a 2-substituted compound, in about 2% yield. The nature of the two main compounds was established by relating them by yield to the crystalline transformation products VIII (55%) and IX (10%), of which the structure and configuration was subsequently elucidated. These products were obtained by treating the mixture of VI and VII with methanol in the presence of a catalytic amount of HCl. A dimethyl ketal (VIII), m.p. 149–150°, was formed from VI, and a ketone (IX), m.p. 127–129°, was formed from VII. The addition of alcohols to enol ethers to form acetals is described in the literature.[7] The formation of the keto ester IX, by hydrolysis of VII, is due to traces of water in the reaction mixture (see Chart II).

Careful hydrolysis of the ketal group in the ketal ester VIII, for which the indicated *cis-anti* configuration was later established, yielded the keto ester XII. The latter could be reconverted into VIII with trimethyl orthoformate and a little acid, indicating that the hydrolysis had not changed the configuration. Saponification of the *cis-anti* ketal ester VIII into the corresponding ketal acid X, and careful hydrolysis of the ketal group of the latter yielded, without change of configuration, the *cis-anti* keto acid XI. This acid could be reconverted into the *cis-anti* keto ester XII

(1) Presented before the Organic Chemical Division at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) Deceased Feb. 17, 1964.

(3) M. W. Goldberg and W. E. Scott, U. S. Patent 2,524,787 (Oct. 10, 1950).

(4) M. S. Newman, *J. Am. Chem. Soc.*, **75**, 4740 (1953).

(5) J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 219 (1948).

(6) (a) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 3058 (1942); (b) H. O. House, W. F. Gannon, R. S. Ro, and D. J. Wluka, *ibid.*, **82**, 1463 (1960); (c) S. B. Needleman and M. C. Chang-Kuo, *Chem. Rev.*, **62**, 405 (1962); (d) V. Georgian and J. Lepe M., *J. Org. Chem.*, **29**, 40 (1964); (e) V. Georgian and J. Lepe M., *ibid.*, **29**, 45 (1964); (f) V. Georgian and L. T. Georgian, *ibid.*, **29**, 58 (1964).

(7) W. J. Croxall, F. J. Glavis, and H. T. Neher, *J. Am. Chem. Soc.* **70**, 2805 (1948).

CHART II

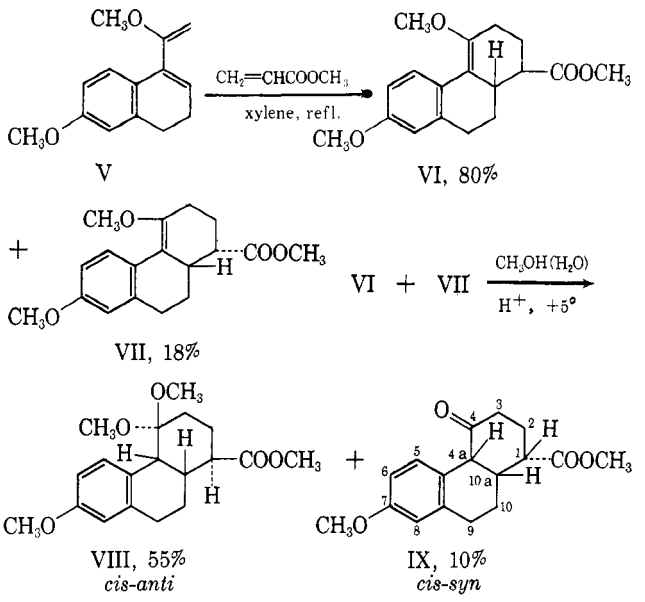
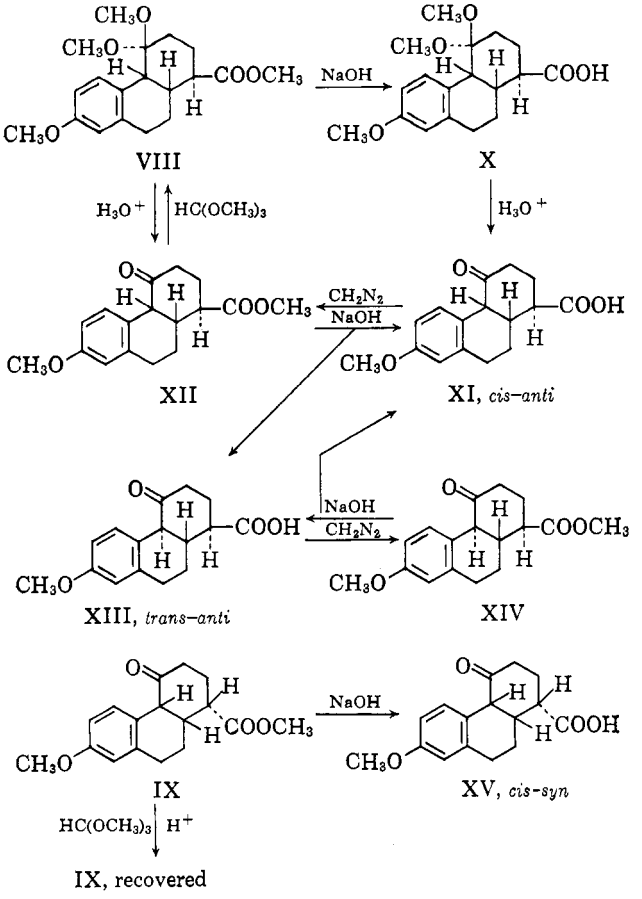


CHART III



with diazomethane in ether. The *cis* or *trans* designations in this paper refer to the relationship of the hydrogens in the 4a- and 10a-positions, whereas the *syn* or *anti* nomenclature refers to the relative configuration of the hydrogens in the 1- and 10a-positions.

The *cis-anti* keto ester XII, upon saponification with refluxing 1 *N* NaOH, yielded approximately equal quantities of the *cis-anti* keto acid XI and the *trans-anti* keto acid XIII. The *trans-anti* keto acid XIII gave with diazomethane the isomeric *trans-anti* keto ester XIV. Saponification of this keto ester XIV in refluxing 1 *N* NaOH yielded an equilibrium mixture of acids, from which the *trans-anti* keto acid XIII and the *cis-anti* keto acid XI were isolated in an approximately 1:1 ratio. The *cis-syn* keto ester IX yielded only one keto acid (XV) upon saponification with 1 *N* NaOH.

The *cis-syn* keto ester IX was recovered unchanged after treatment with trimethyl orthoformate and a little acid. This can be explained by the strong 1,3-diaxial interaction between the 4α-methoxy group of the ketal of IX and the 10,10a-bond. Since the ketal formation is a reversible reaction, this should lead to an equilibrium mixture containing mainly the ketone IX. The *cis-anti* ketal ester VIII, in which no such interaction with the ketal group exists, is readily formed from the *cis-anti* keto ester XII, as already mentioned. Chart III summarizes these results.

To prove the structure and configuration of the compounds, the three isomeric keto esters XIV, IX, and XII were converted into the corresponding desoxo acids XXII, XXIII, and XXIV in a three-step procedure. First they were treated with ethane-1,2-dithiol and boron trifluoride etherate at room temperature, giving the corresponding dithioketals XVI, XVII, and XVIII in good yield. A configurational change in the B/C ring junction can be excluded, since several investigators have shown that the formation of dithioketals proceeds without inversion of configuration.[8a-c] Raney nickel desulfurization yielded the corresponding desoxo esters XIX, XX, and XII, which upon saponification gave the aforementioned desoxo acids XXII, XXIII, and XXIV. The two *cis*-desoxo acids XXIII and XXIV were identified by comparison with preparations obtained by the series of reactions described below.

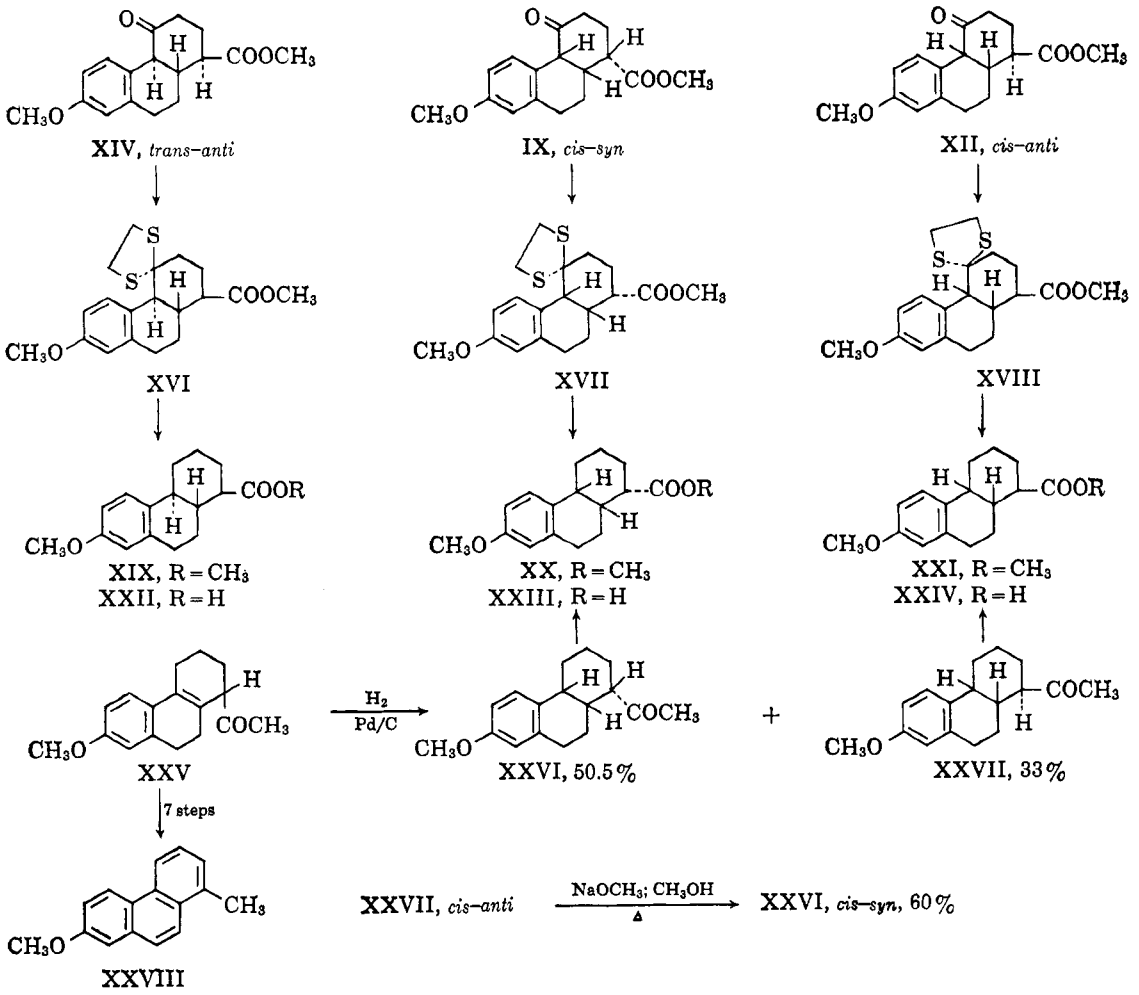
Addition of methyl vinyl ketone to 1-vinyl-6-methoxy-3,4-dihydronaphthalene, followed by rearrangement of the double bond in the mixture of adducts to the more stable 4a,10a-position, yields a mixture of the 2- and 1-substituted methyl ketones, of the hexahydrophenanthrene series, which can be separated.[9] The minor product of the reaction has now been shown to be 1-acetyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XXV) by ultraviolet absorption studies in sodium methoxide–methanol (extended conjugation caused by enolization), by n.m.r. spectroscopy (diffuse triplet at δ 3.25 for the tertiary hydrogen in the 1-position), and also by conversion of the compound into the known[5] 1-methyl-7-methoxyphenanthrene (XXVIII) (see Experimental).

Catalytic hydrogenation of XXV yielded two saturated methyl ketones, XXVI in 50.5% and XXVII in 33% yield. Sodium hypobromite oxidation of XXVI yielded an acid, which was identical with the desoxo acid XXIII, obtained from keto ester IX. Sodium hypobromite oxidation of XXVII yielded another acid, which turned out to be identical with the desoxo acid XXIV, obtained from the keto ester XII. These results are summarized in Chart IV.

(8) (a) J. F. Eastham and G. B. Miles, *J. Org. Chem.*, **25**, 826 (1 60); (b) N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960); (c) R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Am. Chem. Soc.*, **83**, 4006 (1961).

(9) M. W. Goldberg and W. E. Scott, U. S. Patent 2,894,958 (July 14, 1959).

CHART IV



Results and Discussion

It can be assumed that the catalytic hydrogenation of 1-acetyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XXV), using a palladium-on-charcoal catalyst in a neutral medium at room temperature and atmospheric pressure, will predominantly lead to *cis* addition of the hydrogen to the tetrasubstituted double bond, in accordance with similar findings in the literature.[10a-d] It is also to be expected that the adsorption of hydrogen will occur preferentially on the relatively flat side of XXV, *i.e.*, on the side away from the bulky acyl group.[11a-c] The major hydrogenation product (XXVI) should therefore have the *cis-syn*, and the minor product (XXVII) the *cis-anti* configuration.

The *cis-anti* ketone XXVII was inverted into the *cis-syn* ketone XXVI in a 60% yield by refluxing with 2.6 *N* $NaOCH_3$ in methanol. There is no keto group next to the ring junction, therefore the *cis-anti* $\rightleftharpoons$ *cis-syn* relationship of the two isomeric ketones XXVII and XXVI is clearly established. Model studies explain this inversion well, since there are strong 1,3-diaxial interactions in the *cis-anti* ketone XXVII between the C-1 hydrogen and the 4a,4b- and the 9,10 bond. There might also be an interaction between the C-1 and the C-3 hydrogens and the π-electron cloud of the benzene ring in XXVII, which is less likely with the flatter ring arrangement of the *cis-syn* ketone XXVI. Fisher models have been used in the paracyclophane series to determine hydrogen π-electron cloud repulsions.[12]

Since the keto ester IX gave the desoxo acid XXIII, which was obtained from the major hydrogenation product XXVI, IX must have the *cis-syn* configuration. Keto ester XII, on the other hand, must have the *cis-anti* configuration, since it yielded the desoxo acid XXIV, which could also be obtained from the minor hydrogenation product, the *cis-anti* ketone XXVII.

The keto ester XIV must have the *trans-anti* configuration, since it is interconvertible with the *cis-anti* keto ester XII. This was carried out by saponification to a mixture of the corresponding keto acids XI and XIII, followed by separation, and esterification with diazomethane. Enolization in the 4,4a-position with partial inversion at the 4a-position makes this equilibration possible. This finding supports the stereochemistry of XII and (XIV), which was based on the steric course of the hydrogenation reaction. It also indicates that the *cis-anti* and the *trans-anti* configurations are thermodynamically about equally stable, since about equal amounts of the *cis-anti* (XI) and *trans-anti*

(10) (a) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942); (b) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 2318 (1956); (c) R. L. Burwell, *Chem. Rev.*, **57**, 895 (1957); (d) D. K. Banerjee, V. Paul, and S. K. Balasubramanian, *Tetrahedron Letters*, No **12**, 23 (1960).

(11) (a) R. L. Clarke and C. M. Martini, *J. Am. Chem. Soc.*, **81**, 5176 (1959); (b) H. J. E. Loewenthal, *Tetrahedron*, **6**, 269 (1959); (c) J. Castello, E. R. H. Jones, G. D. Meakins, S. Palmer, and R. Swindells, *J. Chem. Soc.*, 2907 (1962).

(12) D. J. Cram and M. Goldstein, *J. Am. Chem. Soc.*, **85**, 1063 (1963).

keto acids (XIII) were found in the equilibrium mixture. This is in agreement with results obtained in the steroid series, where it was shown[13a,b] that an aromatic ring A tends to flatten out the rest of the molecule, which reduces the difference in energy levels to such an extent that rings B and C may exhibit a similar stability with either a *cis* or a *trans* ring fusion. The *cis-syn* configuration, however, represents the most stable structural arrangement in the series of these tricyclic compounds, with or without a keto group in the 4-position.

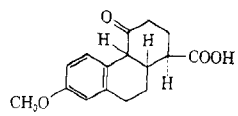
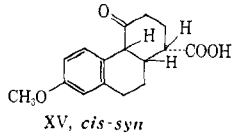
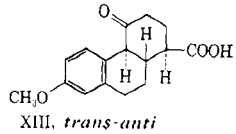
The *cis-syn* configuration of the keto ester IX is further supported by the lack of ketal formation with trimethyl orthoformate and acid, as already mentioned in the first part of this paper.

The β-oriented ester group in VI, the major addition product of the Diels–Alder reaction, is probably due to the rather drastic reaction conditions (refluxing for 72 hr. in xylene). It is known that such conditions increase the amount of *exo* addition products in the reaction mixture.[14a–d]

Further proof for the assumed stereochemistry of these compounds was obtained by n.m.r. spectroscopy, carried out by Dr. E. Billeter of our Physical Chemistry Department. The spectra of the three isomeric keto acids XI, XIII, and XV, were determined at 60 Mc., in perdeuteriopyridine as the solvent and tetramethylsilane as the internal standard. The results are summarized in Table I.

TABLE I

N.M.R. STUDIES OF ISOMERIC KETO ACIDS

Compound	Configuration of the 4a-hydrogen in ring C	N.m.r. signal of the 4a-hydrogen
 XI, *cis-anti*	Equatorial	δ 4.10 Doublet J = 5.0 c.p.s.
 XV, *cis-syn*	Axial	δ 3.90 Doublet J = 5.0 c.p.s.
 XIII, *trans-anti*	Axial	δ 3.88 Doublet J = 12.0 c.p.s.

The 4a-hydrogen was split by the 10a-hydrogen only and appeared therefore as a doublet in all three spectra. The small coupling constant of J = 5.0 c.p.s. for the *cis* compounds, and the large coupling constant of J = 12.0 c.p.s. for the *trans* compound is in good agreement with the relationship between the dihedral angle and the coupling constant of vicinal hydrogens.[13b,15] The chemical shift of the 4a-hydrogen is practically identical in the *cis-syn* (XV) and in the *trans-anti* (XIII) keto acids (δ 3.90 and 3.88). The 4a-hydrogen in these compounds is axial in ring C, and practically perpendicular to the plane of the carbonyl group. In the *cis-anti* keto acid XI, however, the 4a-hydrogen lies practically in the plane of the carbonyl group, and the signal is being shifted downfield (δ 4.10) because of the paramagnetic shielding effect of the carbonyl group.[16a,b]

It should be noted that all compounds described in this paper are racemates. As a matter of convenience, only one enantiomeric series (10aβ-hydrogen) has been pictured.

Experimental[17]

1-Acetyl-3,4-dihydro-6-methoxynaphthalene (III).—Four grams of HgO was stirred at room temperature with 200 ml. of 6 N aqueous H_2SO_4 until a clear solution was obtained. The solution was then poured into 400 ml. of ice–water, 100 g. of Dowex 50W-X8 cation-exchange resin was added, and the mixture was stirred at room temperature for 24 hr. The mercurated resin was then filtered off and washed free of H_2SO_4 with water. It was dried for 1 hr. at room temperature under vacuum and was used for the hydration–dehydration reaction as follows.

Crude, uncrystallized 1-ethinyl-1-hydroxy-6-methoxytetralin[3] (II, 300 g.) was dissolved in 2100 ml. of methanol, 425 ml. of water was added, and a fast stream of nitrogen was bubbled through the stirred solution for about 20–25 min. The mercurated resin was now added to the mixture, which was stirred and refluxed under nitrogen for 72 hr. The resin was then filtered off and washed thoroughly with two 200-ml. portions of hot methanol. The filtrate was concentrated almost to dryness *in vacuo*, and the residue was thoroughly extracted with ethyl acetate. The ethyl acetate solution was washed with brine, dried over Na_2SO_4 and $MgSO_4$, and treated at room temperature with Darco K.B.; the filtered solution was evaporated *in vacuo*. The residual oil crystallized upon addition of 200 ml. of ether. After standing for 16 hr., the crystals were filtered off and washed with approximately 200 ml. of a 1:1 by volume mixture of ether and petroleum ether (b.p. 90–120°) to yield 107 g. of ketone III, m.p. 77–78°.

An additional 13.0 g. of the ketone III, m.p. 76–78°, was obtained from the mother liquor, increasing the yield to 40%, based on crude carbinol II; ultraviolet absorption: λ_{max} 243 mμ (ε 12,200), 286 (5200).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.10; H, 6.96.

1-(1,1-Dimethoxyethyl)-3,4-dihydro-6-methoxynaphthalene (IV).—1-Acetyl-6-methoxy-3,4-dihydronaphthalene (III, 60 g.) was dissolved in 200 ml. of absolute methanol and 50 ml. of trimethyl orthoformate. To this solution was added 0.4 ml. of 4.4 N methylsulfuric acid; the mixture was stirred at room temperature under exclusion of moisture for 2 hr. and then kept in the refrigerator for 16 hr. After adding 15 ml. of 5% NaOH in methanol, the contents of the flask were poured into 400 ml. of ice–water. The mixture was extracted with ether; the ether extract was washed with water, dried over $MgSO_4$, and concentrated *in vacuo* to give 73.5 g. of IV. The product was used without further purification for the next step.

A small sample was recrystallized from methanol, giving pure IV, m.p. 59.5–61.0°; ultraviolet absorption: λ_{max} 270 mμ (ε 12,520), λ_{infl} 300 mμ (ε 1800).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.02. Found: C, 72.03; H, 8.08.

1-(1-Methoxyvinyl)-3,4-dihydro-6-methoxynaphthalene (V).—Anhydrous $KHSO_4$ (0.6 g.) was added to 73 g. of IV; the mixture was kept at 130° and 20 mm. under nitrogen for 1 hr. It was then cooled to room temperature, dry xylene was added, and the solution was filtered. Removal of the xylene gave 63 g. of V (98%), an oil which could be used without further purification for the Diels–Alder reaction.

In one experiment, V was distilled, b.p. 120° (0.03 mm.); $n^{23}D$ 1.5860; ultraviolet absorption: λ_{max} 275 mμ (ε 10,340).

(13) (a) E. J. Bailey, J. Ellis, J. F. Oughton, and L. Stephenson, *J. Chem. Soc.*, 4535 (1961), and examples mentioned therein; (b) H. Hasegawa, S. Nozoe, and K. Tsuda, *Chem. Pharm. Bull.*, **11**, 1037 (1963).

(14) (a) K. Alder, M. Schumacher, and O. Wolff, *Ann.*, **564**, 79 (1949); (b) M. F. Ansell and G. T. Brooks, *J. Chem. Soc.*, 4518 (1956); (c) F. Winternitz and C. Balmossiere, *Tetrahedron*, **2**, 100 (1958); (d) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

(15) M. Karplus, *ibid.*, **85**, 2870 (1963).

(16) (a) O. L. Chapman, H. G. Smith, and R. W. King, *ibid.*, **85**, 806 (1963); (b) D. H. Williams, N. S. Bhacca, and C. Djerassi, *ibid.*, **85**, 2810 (1963).

(17) All melting points were determined in a Thomas-Hoover melting point apparatus and are corrected. All ultraviolet spectra were taken in ethanol.

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.66; H, 7.68.

4,7-Dimethoxy-1,2,3,9,10,10aβ-hexahydro-1β- and -1α-phenanthrenecarboxylic Acid Methyl Ester (VI and VII).—To 63 g. of crude diene V was added 90 ml. of methyl acrylate and 800 ml. of dry xylene. The mixture was refluxed under nitrogen for 72 hr. Xylene and excess methyl acrylate were removed by vacuum distillation, and the residual oil was then fractionated in high vacuum, giving 69.1 g. of addition product, consisting of about 80% of the 1β-ester VI and 18% of the 1α-ester VII. This corresponds to a 76% over-all yield based on 1-acetyl-6-methoxy-3,4-dihydronaphthalene (III). The ratio of VI and VII was determined by gas chromatography on a 1% Carbowax 20M column (6.5 ft.) at 200°, using H_2 (60 ml./min.) and argon (100 ml./min.) flow rate in a Barber Colman apparatus with a Wilkens hydrogen flame ionization detector.

The mixture of VI and VII had b.p. 170–175° (0.03 mm.); $n^{23}D$ 1.5733; ultraviolet absorption: λ_{max} 265 mμ (ε 18,200), λ_{infl} 308 mμ (ε 1600).

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.44; H, 7.37.

4,4,7-Trimethoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid Methyl Ester (VIII) and 4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1-α-phenanthrenecarboxylic Acid Methyl Ester (IX).—The mixture of VI and VII (42.3 g.) was dissolved in 40 ml. of absolute methanol. To the solution was added at once, at +5°, 4 ml. of 0.57 *N* methanolic HCl, and the mixture was kept in the refrigerator for 72 hr. After adding 100 ml. of a 2% $NaHCO_3$ solution, the mixture was extracted with methylene chloride. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crystalline residue was recrystallized from a small amount of methanol, giving 26.2 g. of VIII, m.p. 148–150° (56%); ultraviolet absorption: λ_{max} 224 mμ (ε 8520), 278 (1630); λ_{infl} 286 mμ (ε 1380).

Anal. Calcd. for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.15; H, 7.93.

The mother liquor of VIII was evaporated to dryness *in vacuo*, 20 ml. of 0.06 *N* methanolic HCl was added to the residue, and the mixture was stirred at room temperature for 2 hr. It was then kept in the refrigerator for 16 hr. After adding 50 ml. of 1% $NaHCO_3$ solution, the mixture was extracted with ethyl acetate. The extract was washed with brine, dried over $MgSO_4$, and concentrated to dryness *in vacuo*. Treatment with methanol gave 4.0 g. of IX, m.p. 122–124° (10%). Repeated recrystallization from methanol yielded the analytical sample, m.p. 127–129°; ultraviolet asorption: λ_{max} 219 mμ (ε 9235), 279 (1840), 285 (1640); infrared absorption: ν_{max}^{KBr} 1711 (keto carbonyl), 1725 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.73; H, 6.99. Found: C, 70.72; H, 7.08.

Attempted Ketalization of IX.—To a solution of 1.3 g. of keto ester IX in 10 ml. of methanol was added 4 ml. of trimethyl orthoformate and 2.6 ml. of 2 *N* methylsulfuric acid. The solution was kept at room temperature, protected against moisture, for 16 hr. and was then poured into a mixture of 100 ml. of ice–water and 10 ml. of saturated $NaHCO_3$ solution. The mixture was extracted with methylene chloride; the methylene chloride extract was washed free of acid and dried over calcium chloride. Removal of the solvent *in vacuo* afforded an oil, which was dissolved in a small amount of methanol and triturated with water, giving 0.9 g. of unchanged starting material (IX), m.p. 127–129°.

4,4,7-Trimethoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid (X).—Ketal ester VIII (5.8 g.) was stirred and refluxed under nitrogen in 200 ml. of 1 *N* NaOH for 5 hr. The mixture was cooled to room temperature and extracted with ether to remove any unsaponified material. The basic solution was then cooled and carefully acidified with 2 *N* HCl. The precipitate was taken up in ethyl acetate, and the aqueous solution was re-extracted with ethyl acetate. The combined ethyl acetate solutions were washed with brine, dried over $MgSO_4$, and evaporated to dryness *in vacuo*. Trituration with ether gave 5.0 g. of X (90%), m.p. 125–127° dec. Three recrystallizations from methanol yielded the analytical sample, m.p. 135–136° dec.; ultraviolet absorption: λ_{max} 222 mμ (ε 8420), 278 (1620); λ_{infl} 286 mμ (ε 1330); infrared absorption: ν_{max}^{KBr} 1698 cm.$^{-1}$ (carbonyl of acid).

Anal. Calcd. for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.47; H, 7.67.

4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid (XI) From X.—Ketal acid X (3.6 g.) was refluxed under nitrogen for 1 hr. with 58 ml. of 0.06 *N* methanolic HCl and 2 ml. of water. The mixture was cooled to room temperature and poured into 100 ml. of water; the aqueous mixture was concentrated to about half of its original volume *in vacuo*. The residue was extracted with ethyl acetate; the extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue gave, upon trituration with ether, 2.9 g. (94%) of the crude keto acid XI, m.p. 147–150°. Recrystallization from methanol gave the analytical sample, m.p. 152–153°; ultraviolet absorption: λ_{infl} 220 mμ (ε 8800), 287 (1700); λ_{max} 280 mμ (ε 1920); infrared absorption: ν_{max}^{KBr} 1695 (carbonyl of acid), 1710 cm.$^{-1}$ (keto carbonyl).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.62. Found: C, 70.20; H, 6.55.

4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid Methyl Ester (XII). A. From Keto Acid XI.—The keto acid (400 mg.) was dissolved in 10 ml. of cold methanol and was esterified in the usual manner with an excess of diazomethane in ether. Removal of the solvents *in vacuo* gave an oil that crystallized slowly on standing. Recrystallization from dilute methanol gave 350 mg. of the keto ester XI, m.p. 88–90°; ultraviolet absorption: λ_{max} 220 mμ (ε 9700), 279 (2050); λ_{infl} 287 mμ (ε 1810); infrared absorption: ν_{max}^{KBr} 1710 (keto carbonyl), 1727 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.53; H, 6.93.

B. From Ketal Ester VIII.—The ketal ester (1.0 g.) was suspended in a mixture of 18 ml. of acetone and 1 ml. of water. The suspension was cooled to 0° and 0.05 ml. of concentrated HCl was added. The mixture was stirred for about 5–10 min. at +5° until a solution was obtained. It was then poured into a dilute $NaHCO_3$ solution (3 ml. of saturated $NaHCO_3$ solution in 100 ml. of water). The oily reaction product was extracted with ether; the ether extract was washed with ice–water, dried over $MgSO_4$, and concentrated *in vacuo*, leaving 0.9 g. of a solid. Recrystallization from aqueous methanol gave 0.83 g. of XII, m.p. 88–90°. The product was identical with the compound prepared by method A, as shown by mixture melting point determination and by the identity of the ultraviolet and infrared spectra.

4,4,7-Trimethoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid Methyl Ester (VIII) from Keto Ester XII.—Keto ester XII (1.7 g.) was dissolved in 10 ml. of methanol and 4 ml. of trimethyl orthoformate; 2 ml. of 2 *N* methylsulfuric acid was added, whereupon the mixture crystallized immediately. After standing for 16 hr. at room temperature, the crystals were dissolved by adding methylene chloride, and the solution was poured into 100 ml. of ice-cold 1% $NaHCO_3$ solution. The methylene chloride solution was separated and the aqueous phase once more extracted with methylene chloride. The combined methylene chloride extracts were washed with brine and dried over $CaCl_2$. Concentration *in vacuo* gave a solid residue. Crystallization from acetone gave 1.3 g. of the ketal ester VIII, m.p. 148–150° (66%), identical with the compound obtained *via* addition of methanol to VI.

4-Oxo-7-methoxy-1,2,3,4,4aα,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid Methyl Ester (XIV).—A suspension of 480 g. of keto acid XIII in 20 ml. of methanol was treated with diazomethane in ether. After standing at room temperature for 16 hr., the solvents were evaporated *in vacuo*, leaving a crystalline residue. Recrystallization from methanol gave 460 mg. of keto ester XIV, m.p. 160–161°; ultraviolet absorption: λ_{infl} 220 mμ (ε 9750); λ_{max} 278 mμ (ε 1950), 284 (1800); infrared absorption: ν_{max}^{KBr} 1720 (keto carbonyl), 1740 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.67; H, 6.92.

4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid (XI) and 4-Oxo-7-methoxy-1,2,3,4,4aα,-9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid (XIII). A. From Keto Ester XII.—The keto ester (2.9 g.) was saponified by refluxing under nitrogen in 100 ml. of 1 *N* NaOH for 16 hr. with stirring. The basic solution was extracted with ether to remove unsaponified material. It was cooled in an ice bath and carefully acidified with 2 *N* HCl in the presence of ethyl acetate. The acidified solution was extracted once more with ethyl acetate. The combined ethyl acetate solutions were washed with brine, dried over $MgSO_4$, and concentrated to dryness *in vacuo*, giving

2.8 g. of a solid residue. Recrystallization from methanol gave 0.9 g. of the keto acid XIII in the form of a monohydrate.

The compound could be dehydrated at 100° (0.1 mm.) to yield anhydrous XIII, m.p. 182–183°; ultraviolet absorption: λ_{infl} 220 mμ (ε 7800); λ_{max} 278 mμ (ε 1600), 285 (1540); infrared absorption: ν_{max}^{KBr} 2550–2740 (associated OH of acid), 1710–1725 cm.$^{-1}$ (keto and acidic carbonyl).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.62. Found: C, 69.91; H, 6.94.

The mother liquor of XIII yielded, after standing in the refrigerator for 16 hr., 0.7 g. of the isomeric keto acid XI, m.p. 150–152°. This preparation was identical with the the sample prepared by the hydrolysis of the ketal acid X.

B. From Keto Ester XIV.—Keto ester XIV (1.5 g.) was saponified by refluxing under nitrogen in 100 ml. of 1 *N* NaOH for 3 hr. with stirring. The reaction mixture was worked up as in A to yield 0.5 g. of the keto acid XIII and 0.4 g. of the isomeric keto acid XI, identified by mixture melting point determination and by ultraviolet and infrared spectroscopy.

4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1α-phenanthrenecarboxylic Acid (XV).—The keto ester IX (1.6 g.) was saponified as described for XIV to yield 1.23 g. of crude XV, m.p. 168–171°. Recrystallization from acetone yielded 0.75 g. of the pure keto acid XV, m.p. 179–179.5°; ultraviolet absorption: λ_{infl} 220 mμ (ε 9250); λ_{max} 276 mμ (ε 1780), 285 (1550); infrared absorption: ν_{max}^{KBr} 2500–2700 (associated OH of acid), 1725 (acidic carbonyl), 1710 cm.$^{-1}$ (keto carbonyl).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.18; H, 6.37.

Methyl 4-Oxo-7-methoxy-1,2,3,4,4aα,9,10,10aβ-octahydro-1β-phenanthrenecarboxylate 4-Ethylenethioketal (XVI).—The keto ester XIV (2.5 g.) was dissolved in 5.0 ml. of 1,2-ethanedithiol, and 2.5 ml. of boron trifluoride etherate was added at 0°, within 10 min. After standing for 16 hr. at room temperature, dry benzene was added and the reaction mixture was neutralized by the addition of anhydrous, solid $NaHCO_3$. The benzene solution was filtered and evaporated *in vacuo*, giving 2.85 g. (90.2%) of the thioketal ester XVI, m.p. 92–92.5°. Recrystallization from methanol yielded 2.45 g. of the pure ester XVI, m.p. 93–94°; ultraviolet absorption: λ_{infl} 225 mμ (ε 9400); λ_{max} 276 (1400), 285 (1200); infrared absorption: $\nu_{max}^{CHCl_3}$ 1729 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{19}H_{24}O_3S_2$: C, 62.60; H, 6.64; S, 17.59. Found: C, 62.62; H, 6.66; S, 17.80.

7-Methoxy-1,2,3,4,4aα,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid Methyl Ester (XIX).—The thioketal ester XVI (1.25 g.) was stirred and refluxed in 120 ml. of methanol with 20 g. of Raney nickel for 16 hr., after which the solution was filtered through Hyflow-Supercel under a cover of CO_2. The filtrate was concentrated *in vacuo*, giving 0.9 g. of the crystalline deoxo ester XIX. Recrystallization from ligroin (b.p. 90–120°) yielded 0.62 g. of the pure ester XIX, m.p. 112–113°; ultraviolet absorption: λ_{max} 220 mμ (ε 8000), 278 (1970), 286 (1810); infrared absorption: $\nu_{max}^{CHCl_3}$ 1729 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.34; H, 8.22.

7-Methoxy-1,2,3,4,4aα,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid (XXII).—The desoxo ester XIX (500 mg.) was refluxed with 30 ml. of 1 *N* NaOH for 3 hr. The solution was then cooled, unsaponified material was extracted with ether, and the aqueous layer was acidified with 2 *N* HCl and extracted with ethyl acetate. The extract was washed with brine, dried over $MgSO_4$, and concentrated to dryness *in vacuo*, giving 397 mg. of crude XXII. Recrystallization from acetonitrile yielded 372 mg. of the pure desoxo acid XXII, m.p. 143–144°; ultraviolet absorption: λ_{max} 221 mμ (ε 8200), 278 (ε 2000), 287 (1870); infrared absorption: ν_{max}^{KBr} 1695 cm.$^{-1}$ (carbonyl of acid).

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.49; H, 7.85.

Methyl 4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1α-phenanthrenecarboxylate 4-Ethylenethioketal (XVII).—Keto ester IX (6.9 g.) was dissolved in 14 ml. of 1,2-ethanedithiol, and 14 ml. of borontrifluoride etherate was added at 0°. The reaction mixture was treated as in the preparation of XVI, giving 5.5 g. of the isomeric thioketal ester XVII, m.p. 116–117°, after recrystallization from methanol; ultraviolet absorption: λ_{max} 278 mμ (ε 1870), 285 (1830); infrared absorption: $\nu_{max}^{CHCl_3}$ 1728 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{19}H_{24}O_3S_2$: C, 62.60; H, 6.64; S, 17.59. Found: C, 62.75; H, 6.87; S, 17.51.

7-Methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1α-phenanthrene carboxylic Acid Methyl Ester (XX).—Thioketal ester XVII (5.5 g.) was stirred and refluxed in 350 ml. of methanol with 150 g. of Raney nickel for 16 hr. The reaction mixture was worked up as in the preparation of the isomeric ester XIX, giving 4.15 g. of an oil, which crystallized on standing at room temperature. Recrystallization from 90% methanol afforded the pure ester XX, m.p. 64–66°; ultraviolet absorption: λ_{max} 220 mμ (ε 7870), 279 (1950), 287 (1850); infrared absorption: $\nu_{max}^{CHCl_3}$ 1728 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.74; H, 8.18.

7-Methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1α-phenanthrenecarboxylic Acid (XXIII). A. By Saponification of XX.—Desoxo ester XX (4.0 g.) was stirred and refluxed with 120 ml. of 1 *N* NaOH for 3 hr. The reaction mixture was worked up as in the preparation of XXII, giving 3.5 g. of the desoxo acid XXIII. Recrystallization from acetonitrile yielded the pure acid, m.p. 160–161°; ultraviolet absorption: λ_{max} 220 mμ (ε 8010), 279 (2000), 287 (1900); infrared absorption: $\nu_{max}^{CHCl_3}$ 3500 and 2550–2710 (acidic OH), 1695 cm.$^{-1}$ (carbonyl of acid).

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.64; H, 7.85.

B. From 1α-Acetyl-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydrophenanthrene (XXVI) by Oxidation.—A solution of sodium hypobromite was prepared from 2.5 g. of NaOH and 1.1 ml. of bromine in 33 ml. of water. To this cooled solution was added within 1.5 hr. at 0–5° with stirring 1.5 g. of the *cis-syn* methyl ketone XXVI dissolved in 33 ml. of dioxane. The reaction mixture was worked up as in method B for the preparation of XXIV, giving, after recrystallization from acetonitrile, 1.25 g. (83%) of the desoxo acid XXIII, m.p. 160–161°. The product was identical (melting point and ultraviolet and infrared spectra) with the preparation obtained from ester XX by method A.

Methyl 4-Oxo-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylate 4-Ethylenethioketal (XVIII).—Keto ester XII (5.0 g.) was treated with 10 ml. of 1,2-ethanedithiol and 10 ml. of borontrifluoride etherate, as in the preparation of XVI, giving 4.7 g. of the thioketal ester XVIII, m.p. 98–99°, after recrystallization from methanol; ultraviolet absorption: λ_{max} 277 mμ (ε 1650), 285 (1550); infrared absorption: ν_{max}^{KBr} 1727 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{19}H_{24}O_3S_2$: C, 62.60; H, 6.64; S, 17.58. Found: C, 62.36; H, 6.63; S, 17.31.

7-Methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid Methyl Ester (XXI).—Thioketal ester XVIII (4.7 g.) was stirred and refluxed in 400 ml. of methanol with 100 g. of Raney nickel for 16 hr. The reaction mixture was worked up as in the preparation of the isomeric ester XIX, giving 3.5 g. of desoxo ester XXI, a colorless oil; $n^{23}D$ 1.5413; infrared absorption: $\nu_{max}^{CHCl_3}$ 1725 cm.$^{-1}$ (ester carbonyl).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.54; H, 8.20.

7-Methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydro-1β-phenanthrenecarboxylic Acid (XXIV). A. By Saponification of XXI.—Desoxo ester XXI (2.2 g.) was stirred and refluxed with 60 ml. of 1 *N* NaOH for 3 hr. The reaction mixture was worked up as in the preparation of XXII, giving 2.0 g. of the crude acid. Recrystallization from acetonitrile gave 1.25 g. of the pure acid XXIV, m.p. 135–137° (60%); ultraviolet absorption: λ_{max} 220 mμ (ε 6890), 280 (1720), 287 (1680); infrared absorption: $\nu_{max}^{CHCl_3}$ 3500 and 2710–2550 (acidic OH), 1700 cm.$^{-1}$ (carbonyl of acid).

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.92; H, 7.48.

B. From 1β-Acetyl-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydrophenanthrene (XXVII) by Oxidation.—A solution of sodium hypobromite was prepared from 13 g. of NaOH and 6.4 ml. of bromine in 175 ml. of water. To this cooled solution was added within 1.5 hr. at 0–5°, with stirring, 9.0 g. of the *cis-anti* methyl ketone XXVII, dissolved in 175 ml. dioxane. When the addition was complete, the cooling bath was removed and the mixture was stirred at room temperature for 1 hr. It was then concentrated to about one-third of its original volume *in vacuo* and was then diluted with 200 ml. of water. This solution was extracted with ether to remove neutral material. It was then cooled and acidified with 2 *N* HCl and extracted again with ether. The ether extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*, giving 8.5 g. of crude acid. Recrystallization from acetonitrile gave 5.3 g. (58%) of the pure acid XXIV, m.p.

135–137°. This preparation was in every respect identical with the product obtained from XXI, as described under A.

1-Acetyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XXV).—Addition of methyl vinyl ketone to 1-vinyl-6-methoxy-3,4-dihydronaphthalene, followed by rearrangement of the 4,4a-double bond into the more stable 4a,10a-position, yielded 2-acetyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene as the main addition product.[9] Careful fractional crystallization of the mother liquors permitted also the isolation of the 1-isomer XXV in a very small yield (1.5%), m.p. 86–87°, after recrystallization from petroleum ether[18]; ultraviolet absorption: λ_{max}^{MeOH} 274 mμ (ε 15,500); in 1 *N* NaOMe–methanol solution after 2 hr. at 65°, λ_{max} 241 mμ (ε 10,400), λ_{min} 275 mμ (ε 5300), λ_{max} 329 mμ (ε 13,120). Under the same conditions the ultraviolet absorption spectrum of the 2-isomer remains practically unchanged. The n.m.r. spectrum of XXV in $CDCl_3$, at 60 Mc., with TMS as internal standard showed δ 3.25 (diffuse triplet) for the C-1 hydrogen.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.87; H, 7.48.

1α-Acetyl-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydrophenanthrene (XXVI) and 1β-Acetyl-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydrophenanthrene (XXVII).—1-Acetyl-7-methoxy-1,2,3,4,-9,10-hexahydrophenanthrene (XXV, 2.6 g.) was hydrogenated at atmospheric pressure and room temperature in 18 ml. of ethyl acetate in the presence of 250 mg. of a 10% palladium-on-carbon catalyst. After the uptake of 1 mole of hydrogen, the catalyst was filtered off, and the ethyl acetate solution was evaporated to dryness *in vacuo*, giving 2.6 g. of a colorless oil. A small amount (0.8 ml.) of ligroin (b.p. 90–120°) was then added to the oil, which crystallized upon scratching with a glass rod. The solid was recrystallized, without removal of the ligroin, from 4 ml. of ethanol. After standing for 2 hr. at room temperature, 0.7 g. of the *cis-anti* methyl ketone XXVII, m.p. 89–91°, was filtered off. One more recrystallization from ethanol afforded the analytical sample, m.p. 91–92°; ultraviolet absorption: λ_{max} 220 mμ (ε 8900), 279 (2280), 288 (ε 2130); infrared absorption: $\nu_{max}^{CHCl_3}$ 1710 (ketone), 1268 cm.$^{-1}$ (ether band).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.97; H, 8.80.

The mother liquor of XXVII was evaporated to dryness *in vacuo*, giving 1.9 g. of an oil, which solidified on standing, m.p. 60–81°. Repeated chromatography of the solid on neutral aluminum oxide (Woelm, grade IV) afforded 0.157 g. of XXVII, m.p. 90–92°, and 1.31 g. of the *cis-syn* methyl ketone XXVI, m.p. 72–74°; ultraviolet absorption: λ_{max} 220 mμ (ε 8800), 278 (2260), 286 (2170); infrared absorption: $\lambda_{max}^{CHCl_3}$ 1710 cm.$^{-1}$ (ketone).

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

Epimerization of XXVII under Basic Conditions.—The *cis-anti* methyl ketone XXVII (1.5 g.) was refluxed under nitrogen in a 2.6 *N* methanolic sodium methoxide solution for 25 min. The solution was poured into ice–water and extracted with ether. The ether extract was washed with water, dried over $MgSO_4$, and evaporated *in vacuo*. Ligroin (10 ml., b.p. 90–120°) was then added to the oily residue, which crystallized on scratching with a glass rod, giving 0.9 g. (60%) of the *cis-syn* methyl ketone XXVI, m.p. 70–72°.

1-Methyl-7-methoxyphenanthrene (XXVIII) from 1-Acetyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene (XXV).—The methyl ketone XXV was first converted into the acid XXIII, as already described. The acid XXIII was converted with diazomethane in ether into the already described methyl ester XX. The ester XX (2.68 g.) was reduced with 1.0 g. of $LiAlH_4$ in 30 ml. of refluxing ether for 1 hr. Ethyl acetate (15 ml.) and saturated Na_2SO_4 solution (15 ml.) were then added carefully. The solution was filtered and the precipitate washed with hot ethyl acetate. The ethyl acetate extract was dried and concentrated *in vacuo*, giving 1.8 g. of the oily 1α-hydroxymethyl-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydrophenanthrene. This alcohol was identified by ultraviolet and infrared analysis and was converted without further purification into the corresponding tosylate. For this purpose, 1.3 g. of the alcohol was treated at 0° in 4 ml. of pyridine with 2.0 g. of *p*-toluenesulfonyl chloride. After standing for 2 hr. at 0° and 16 hr. at +20°, the solution was poured into ice–water, which was extracted with ethyl acetate and with ether. The combined extracts were washed with ice-cold 1 *N* HCl and then with brine, dried over $MgSO_4$, treated with activated carbon, filtered, and evaporated *in vacuo*, giving 1.63 g. of an oil, the *p*-toluenesulfonate of the foregoing alcohol; infrared absorption: $\nu_{max}^{CHCl_3}$ 1170 and 1350 cm.$^{-1}$ (sulfonate bands), no OH-band in the spectrum.

The tosylate (1.6 g.) was refluxed with 0.7 g. of $LiAlH_4$ in 25 ml. of tetrahydrofuran for 16 hr. The reaction mixture was worked up as in the previous $LiAlH_4$ reduction and gave 0.8 g. of an oil, 1α-methyl-7-methoxy-1,2,3,4,4aβ,9,10,10aβ-octahydrophenanthrene, $n^{24}D$ 1.3990; ultraviolet absorption: λ_{max} 278 mμ (ε 2100), 286 (1980).

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.39; H, 9.21.

To 390 mg. of this octahydrophenanthrene derivative was added 0.2 g. of 10% palladium on carbon, and the mixture was heated under a slow stream of nitrogen to 305° within 20 min. The reaction mixture was kept between 305 and 310° for 30 min. It was then cooled to room temperature, and the residue was taken up in ether. The solution was dried over $MgSO_4$, filtered, and evaporated *in vacuo*, giving 314 mg. of crude crystalline material.

Recrystallization from isopropyl alcohol yielded 40 mg. of analytically pure 1-methyl-7-methoxyphenanthrene (XXVIII), m.p. 132.5–133°, which was, according to mixture melting point determination and ultraviolet and infrared spectroscopy, identical with an authentic sample obtained by the procedure described in the literature[5,19]; ultraviolet absorption: λ_{max} 221 mμ (ε 22,800), 231 (19,200), 258 (9000), 322 (635), 331 (500), 337 (1090), 353 (1100).

Acknowledgment.—We are indebted to Dr. V. Toome for the ultraviolet and to Mr. S. Traiman for the infrared spectroscopic data, and to Dr. Steyermark and his staff for the microanalyses. We wish also to express our thanks to Mr. J. Trawinski, Mr. D. Parrish, and Mr. C. Parios for their technical assistance in this investigation.

(18) This compound was first observed by Dr. W. E. Scott of our Research Division.

(19) This sample was obtained from Dr. W. E. Scott of our Research Division.