Synthesis and Solvolytic Rearrangement of Epimeric 4-Methanesulfonyloxy-4a-methyl-*trans*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene and Their 7-Methoxy and 1,1-Dimethyl Derivatives. Conformationally Rigid Homobenzylic Systems

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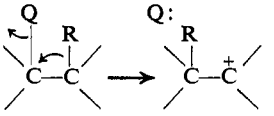
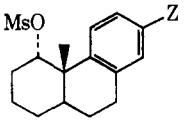
Abstract: The title compounds have been synthesized and their solvolytic rearrangements have been investigated.

Central to many of the unanswered questions[1-3] concerning rearrangements that accompany terpene biosynthesis lies that of the nature of cationic 1,2 alkyl and hydrogen shifts of the type

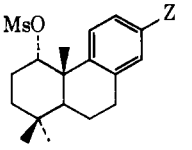


(1)

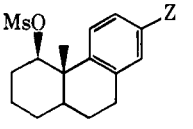
The extent to which rearrangements of this type are inherently susceptible to steric and electronic acceleration, their "concertedness," is of obvious importance in defining the nature of their enzymatic control. The degree to which one can construct suitable solvolytic models of naturally occurring carbonium ion processes is problematical. We have nevertheless synthesized and examined the solvolytic behavior of the six methanesulfonates **1**, **1a**, **2**, **2a**, **3**, and **3a**. These substrates



1, Z = H
a, Z = OMe



2, Z = H
a, Z = OMe



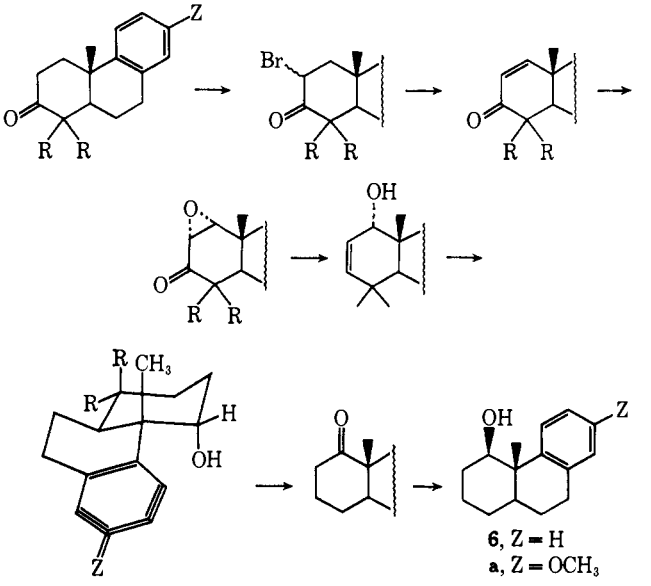
3, Z = H
a, Z = OMe

were chosen for the following reasons. The presence of trans ring fusions affords a relatively rigid substrate geometry, except for the possibility of chair–boat interconversion in the ring bearing the leaving group. Moreover the orientation of the leaving group relative to the aromatic ring is such that aryl participation in solvolysis should be minimized. The resulting passive nature of the aryl group allows its effect on solvolytic alkyl migration to be analyzed in a straightforward manner. Introduction of methyl groups into a 1,3-diaxial relationship with the angular methyl (**2** *vs.* **1**) allows the influence of relief of nonbonded strain on solvolysis rates to be examined. It appears from our work to be described below that although the stereochemical behavior of these compounds on solvolysis is consistent with a concerted 1,2 migration accompanying departure of the leaving group, the rates are remarkably insensitive to relief of strain (**2** *vs.* **1**) or substituent effects (**1a** *vs.* **1**, **2a** *vs.* **2**).

Results and Discussion

Synthesis of substrates and solvolysis products proceeded along classical lines (Scheme I). The stereochemistry of the final tricyclic axial alcohols is defined by (a) the established trans ring fusion of the starting tricyclic ketones, all of which are known compounds (see Experimental Section) and all of whose ring junctions' stereochemistry are well defined as trans, and (b) the stereochemistry of epoxidation of the unsaturated ketone. There are several published examples of the synthesis of 1α-hydroxy steroids by this route[4-6] and there is good reason to expect initial axial nucleophilic attack on the unsaturated ketone to afford the indicated stereochemistry. Moreover the nmr spectra of the set

Scheme I. Synthetic Scheme for Synthesis of Solvolysis Substrates[a]



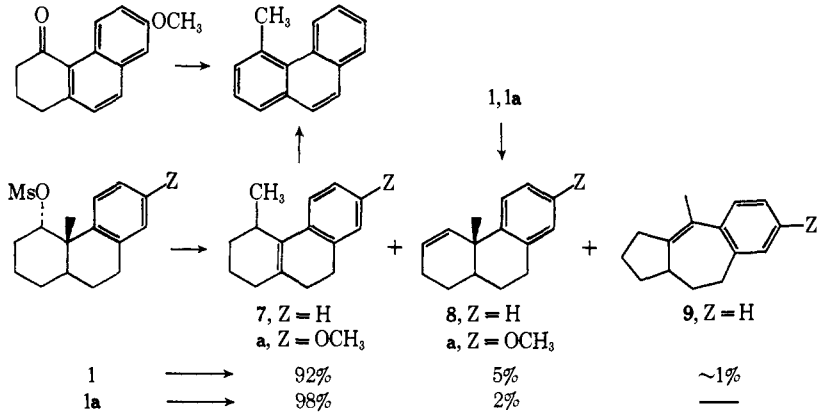
4, R = H; Z = H
a, R = H; Z = OCH_3
5, R = CH_3; Z = H
a, R = CH_3; Z = OCH_3

6, Z = H
a, Z = OCH_3

[a] One enantiomer of each structure is illustrated.

(1) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, **38**, 1890 (1955).
(2) W. Parker, J. S. Roberts, and R. Ramage, *Quart. Rev., Chem. Soc.*, **22**, 331 (1968).
(3) R. B. Clayton, *ibid.*, **19**, 168, 201 (1965).
(4) C. Djerassi, D. H. Williams, and B. Berkuz, *J. Org. Chem.*, **27**, 2205 (1962).
(5) H. Tada and Y. K. Sawa, *ibid.*, **33**, 3347 (1968).
(6) P. S. Wharton, *ibid.*, **26**, 4781 (1961).

Scheme II. Product Mixture Arising from Acetolysis of Methanesulfonates **1** and **1a**

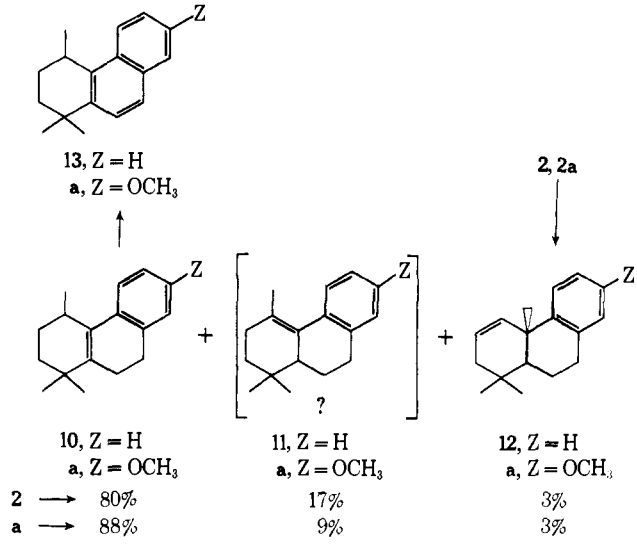


of compounds are in all cases consistent with the presence of a CHOR part structure possessing an axially disposed oxygen.[7] The equatorial alcohol precursors (**6** and **6a**) of **3** and **3a** were prepared by oxidation of **4** and **4a** followed by aluminum isopropoxide reduction of the resulting ketones. It is relevant to the presumed all-chair conformation of these compounds to point out that the nmr spectra showed that all of the "axial" alcohols and their derivatives did in fact possess axial oxygens (equatorial C*H*OR's) and that the "equatorial" alcohols and methanesulfonates possessed equatorial oxygens. A marked deshielding of one of the aromatic hydrogens (presumably that at C-5) in the nmr spectra of **6** and **6a** by the equatorial oxygen is consistent with the assigned stereochemistry.[8] It is interesting that direct equilibration shows the axial alcohol **4** to be *more* stable than the equatorial alcohol **6**.[9] The rate of acetolysis of the methanesulfonate **3** is greater than that of **1**. This is the reverse of the usual axial:equatorial ratio and presumably reflects the nonbonded interaction between the oxygen atom of **3** and the hydrogen at C-5.

Acetolysis of **1** in refluxing acetic acid containing sodium acetate afforded a mixture of seven components of which only two, A (92%) and B (5%), were present in greater than 1% yield. The major product possessed a secondary methyl group, CH_3CH, and a styrene chromophore. Its assigned structure, **7** (Scheme II), arising from methyl migration is confirmed by 2,3-dichloro-5,6-dicyanoquinone (DDQ) dehydrogenation of it to a 4:1 mixture of 4-methylphenanthrene and phenanthrene. The 5% product cochromatographed on glc with a sample of **8** prepared by treatment of **1** with potassium *tert*-butoxide, and corresponds to the product of a simple elimination reaction. One of the minor products, C, 0.9% yield, is tentatively assigned the structure of the major solvolysis product from the epimeric methanesulfonate **3** (see Scheme II) on the basis of peak enhancement in glc. Acetolysis of **1a** afforded a 98:2 mixture of olefins. The 2% component was not isolated but behaved on glc as a sample of the elimination product **8a**. The major product, **7a**, was isolated by recrystallization of the crude crystalline olefin mixture. It too possessed a styrene chromophore in its ultraviolet spectrum and, by its nmr spectrum, a secondary methyl group coupled to a single allylic hydrogen (δ 2.85). DDQ dehydrogenation of the solvolysis olefin mixture afforded 2-methoxy-5-methylphenanthrene, identified by comparison with a sample synthesized as shown in Scheme II.

Acetolysis of the *gem*-dimethyl substituted methanesulfonates **2** and **2a** afforded analogous products. From **2** there was isolated a mixture of three olefins, A, B, and C, in the ratio 80:17:3 (Scheme III). The

Scheme III. Products Arising from Acetolysis of **2** and **2a**

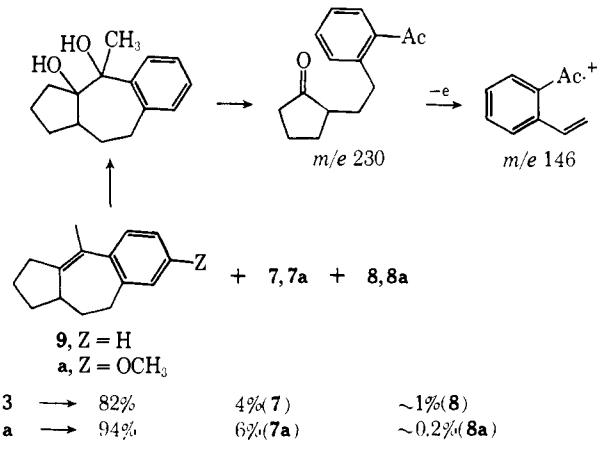


3% component was tentatively assigned structure **12** on the basis of glc comparison of it and an authentic sample; the 17% component remains unidentified but on the basis of the spectra of the crude product may have the structure **11**; the major product, A, 80%, was shown to possess two quaternary and one secondary methyl group and a styrene chromophore. Dehydrogenation of the olefin mixture with DDQ afforded a tetrahydrophenanthrene possessing a secondary methyl and two quartenary methyls. The structure of the major product is accordingly assigned as **10**. Similarly **2a** afforded an olefin mixture: A (88%), B (9%), and C (3%). C was identified by cochromatography as **12a**; B was unidentified but may have a structure **11a** analogous to **11**; and A, possessing a styrene chromophore and one secondary methyl group, and being dehydrogenated to a trimethylmethoxytetrahydrophenanthrene (**13a**), is assigned structure **10a**, this arising by simple methyl migration.

(7) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 80.
(8) R. F. Zucher, *Helv. Chim. Acta*, 46, 2054 (1963).
(9) See, for a possible example, J. W. Huffman, D. M. Alakan, T. W. Bethea, and A. C. Ruggles, *J. Org. Chem.*, 29, 2963 (1964).

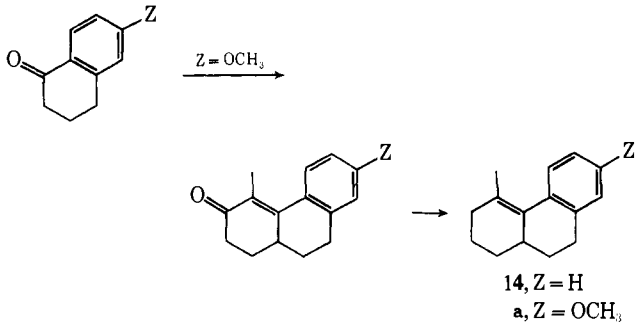
In contrast with the above results, acetolysis of the equatorial methanesulfonate **3** resulted in almost no methyl migration (Scheme IV). In addition to two

Scheme IV. Products Arising from Acetolysis of **3** and **3a**



minor products, present in 4 and 1% and which co-chromatographed with **7** and **8**, respectively, there was isolated a major olefin (82% of the crude solvolysis mixture) assigned structure **9**. In addition to a styrene chromophore, **9** appeared to possess an allylic methyl group. Hydroxylation (OsO_4) followed by periodate cleavage of the resulting diol afforded an oily diketone. The presence of five-membered ring ($\lambda_{max}^{CHCl_3}$ 5.78 μ and conjugated, $\lambda_{max}^{CHCl_3}$ 5.95 μ) ketones coupled with the mass spectral[10] cracking pattern of the diketone allows a reasonably confident assignment of structure **9** to the major solvolysis product. Olefin **14** was ruled out as the solvolysis product by the spectral properties of the diketone and by synthesis (Scheme V) of **14a** and com-

Scheme V



parison of it with the solvolysis mixture. This latter olefin could not be separated by glc from the major olefin on acetolysis of **1a** but could not be detected in the nmr spectrum of the olefin mixture from acetolysis. It must accordingly be a minor product at most. Acetolysis of **3a** proceeded analogously to form a major (94%) olefin (**9a**) possessing properties very similar to those of **9** and two minor olefins, 5.7 and ~0.2%, that cochromatographed with **7a** and **8a**, respectively.

The above results are summarized in Table I and acetolysis rates and activation parameters determined are tabulated in Table II.

The geometry of our substrates, in particular the trans ring fusion and the dihedral angle of approxi-

(10) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden Day, San Francisco, Calif., 1967, pp 129–162.

Table I. Stereochemical Outcome of Acetolysis of Indicated Methanesulfonates[a]

Compd	Anti[c] alkyl migration	Syn[d] alkyl migration	Elimination, %
1, Z = H	92	~1	4.8
a, Z = OMe	98		2.3
2, Z = H	97[b]		3
a, Z = OMe	97[b]		3
3, Z = H	82	3.9	0.8
a, Z = OMe	94	5.7	~0.2

[a] OMS = OSO_2CH_3. [b] Approximately 10% of an unidentified olefin is included in this total (see Discussion). [c] The anti parallel group. [d] The gauche oriented substituent.

mately 60° about C-4, C-4a, C-4b, C-5, ensures that aryl interaction with a positive charge at C-4 should be minimized. In fact no aryl migration is detected on solvolysis of any C-4 epimeric methanesulfonates. These results are to be compared with the acetolysis of neophyl toluenesulfonate which proceeds with almost no (~0.3%) methyl migration.[11] Acetolysis of all of the methanesulfonates afforded, however, a high degree of alkyl rearrangement (Schemes II and III). No acetates were detected and the unrearranged olefins comprised approximately 3–5% of the total solvolysis product mixture. The solvolytic rearrangements thus proceed with a high degree of stereospecificity wherein the trans antiplanar group migrates to produce initially a benzyl carbonium ion (Table I). The stereospecificity is not complete however. The axial methanesulfonate **1** affords approximately 1% of the olefin **9** while the equatorial methanesulfonate **3** affords ~4% of the product **7** arising from methyl migration.[12]

Electronic acceleration of these solvolyses is minimal. The effect of introduction of a para methoxy substituent onto the aromatic ring is to affect a rate enhancement of ~2.2 in the **1**–**1a** series, ~1.8 in the **2**–**2a** series, and essentially nothing in the equatorial methanesulfonates. The effect of introduction of a geminal dimethyl substituent at C-1 is also small; a rate enhancement of ~1.6 in the protio series and ~1.5 in the para methoxy series. Solvolysis of compounds of the above type with predominent migration of the anti alkyl group is in general well precedented.[13,14] In particular Shoppee, *et al.*, have examined the solvolytic behavior (in aqueous acetone) of 1α- and 1β-toluenesulfonyloxy-5α-cholestane.[15] Except for the absence of solvent-captured species in our product mixtures the two cases are similar in that solvolytic migration of the trans methyl group predominates.

Our data do not allow us to distinguish between two limiting mechanistic possibilities. On the one hand we may argue that the stereochemical results are consistent with methyl migration occurring concerted with departure of the leaving group. If this is correct there must be little positive charge on the benzylic carbon in the transition state and little relief of strain arising from

(11) W. H. Saunders, Jr. and R. H. Paine, *J. Amer. Chem. Soc.*, **83**, 882 (1961).

(12) The *ca.* 10% yield product from the methyl-substituted methanesulfonates are assumed to arise from methyl migration.

(13) D. N. Kirk and M. P. Hartshorn, "Reaction Mechanisms in Organic Chemistry," Vol. 7, Elsevier, New York, N. Y., 1968.

(14) C. Heathcock and R. Ratcliffe, *Chem. Commun.*, 11 (1969).

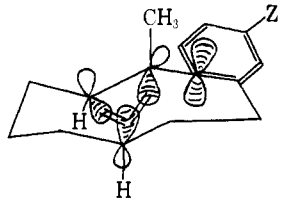
(15) C. W. Shoppee, R. E. Lack, S. C. Sharma, and L. R. Smith, *J. Chem. Soc. C*, 1155 (1967).

Table II. Solvolysis Rates and Activation Parameters for Acetolysis of the Indicated Methanesulfonates

Methanesulfonate	k_{rel} (75°)	T, °C	$k \times 10^5$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	1	59.80 ± 0.01	0.893 ± 0.03		
1	1	72.14 ± 0.01	3.45 ± 0.09		
1		82.19 ± 0.0	12.4 ± 0.02	28.7 ± 1	+3.9 ± 3
3	10 (70°)	69.99 ± 0.01	34.8 ± 0.70		
2	1.8	59.81 ± 0.01	1.73 ± 0.04		
		69.96 ± 0.01	5.52 ± 0.09		
		79.40 ± 0.01	17.5 ± 0.4	28.2 ± 0.8	+3.7 ± 2.4
2a	3	59.81 ± 0.01	3.26 ± 0.06		
		69.96 ± 0.01	10.1 ± 0.3		
		79.40 ± 0.01	30.7 ± 0.7	26.0 ± 0.7	−1.2 ± 2.1
1a	2.2	59.80 ± 0.01	2.19 ± 0.06		
		73.08 ± 0.01	9.08 ± 0.05		
		82.19 ± 0.01	27.21 ± 0.50		
		82.76 ± 0.01	27.43 ± 0.20	25.7 ± 0.7	−2.9 ± 2.1
3a	7.5 (70°)	69.99 ± 0.01	25.15 ± 0.15		

the 1,3-methyl–methyl interaction. The approximate constancy of the ratio of elimination product to rearrangement product is consistent with a concerted process with a lopsided transition state but one must explain away the leakage syn migration as competing classical carbonium ion processes or stereoelectronically bad concerted reactions.

Alternatively one may invoke rate-determining ionization to a tight ion pair followed by collapse of this to the observed products. The small rate acceleration of the para methoxy group is about what one would expect for the absence of interaction between the aromatic ring and the developing positive charge.[16] One must qualify this however by pointing out that the effect of the para methoxy group on the equatorial methanesulfonates' solvolysis rates is appreciably less than on the axial ones'. It would be dangerous however to ascribe this difference to a concerted solvolytic rearrangement wherein the developing benzylcarbonium ion must be poorly stabilized in the equatorial case (*e.g.*, **15**). The rigid geometry of these molecules, with the resulting difference in orientation of the aromatic ring with respect to the leaving group bearing carbon, would require that, to the extent that the inductive effect of the aromatic ring represents a weak π interaction between the developing homobenzyliccarbonium ion and the aromatic ring (C-4b), the inductive effect be dependent



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on the geometry of the molecule as a whole. One could in fact argue that this weak π interaction would be stronger in the axial than in the equatorial cases. The small effect of introduction of an axial methyl–methyl interaction is consistent with the ion pair mechanism, a slight distortion of the ring[17] due to a methyl buttressing effect which is relieved on movement of the methanesulfonate away from the ring. The role of ion pairs in controlling the stereochemistry of attack at the positive center is well documented.

All in all we feel that either explanation suffices to explain our data, with the latter ion pair one being the preferable. Regardless of this, however, solvolysis of these secondary methanesulfonates with alkyl migration is a process that is relatively insensitive to either electronic or steric acceleration. The relevence to backbone rearrangements is then that steric acceleration of these rearrangements, *via* either intra- or intermolecular interactions, seems unlikely to play an important role in the natural event.

Experimental Section[18]

trans-**7-Methoxy-3a-bromo-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (17a).** To a solution of 2.99 g (0.011 mol) of *trans*-7-methoxy-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)phenanthrone[19] in 200 ml of ether was added a solution of 0.43 ml (0.011 mol) of bromine in 75 ml of ether. The reaction mixture was stirred at −78° for 3 hr, allowed to warm to room temperature over 1.5 hr, and worked up. Chromatography of the crude oil on silica gel afforded 2.65 g (69% yield) of bromo ketone **17a** as a viscous oil. Its nmr spectrum suggested that it was a mixture of epimers.

Anal. Calcd for $C_{18}H_{23}O_2Br$: C, 61.54; H, 6.60; Br, 22.75. Found: C, 61.54; H, 6.60; Br, 22.71.

Similarly prepared were compounds **16a**, **16**, and **17**.

trans-**7-Methoxy-3a-bromo-4a-methyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (16a)** exhibited the following characteristics: mp 141–142° (ether); δ ($CDCl_3$) 4.91 (1 H, double d, $J_{3,4ax}$ = 10 Hz, $J_{3,4eq}$ = 6.5 Hz, C*H*Br), from 7-methoxy-4a-methyl-1,4,4a,9,10,-10a-hexahydro-2(3*H*)-phenanthrone.[20]

Anal. Calcd for $C_{16}H_{18}O_2Br$: C, 59.45; H, 5.93; Br, 24.72. Found: C, 59.20; H, 5.94; Br, 24.88.

trans-**3a-Bromo-4a-methyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (16)** exhibited the following characteristics: mp 141–142° (ether); δ ($CDCl_3$) 4.90 (H, double d, $J_{3,4ax}$ = 12 Hz, $J_{3,4eq}$ = 6.5 Hz, C*H*Br), from 4a-methyl-1,4,4a,9,10,10a-hexahydro-2-(3*H*)-phenanthrone.[21]

Anal. Calcd for $C_{15}H_{17}OBr$: C, 61.45; H, 5.84; Br, 27.27. Found: C, 61.50; H, 5.96; Br, 27.22.

trans-**3a-Bromo-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (17)** exhibited the following characteristics: a broad melting solid, mp 87–147° (ether–hexane), apparently a mix-

(16) For the related *cis*- and *trans*-2-arylcyclopentyl case see C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4286, 4287 (1969).

(17) E. L. Eliel, S. H. Schroeter, T. J. Brett, T. J. Brett, F. J. Biros, and J-C Richer, *ibid.*, **88**, 3327 (1966).

(18) Nmr spectra were determined at 60 MHz unless otherwise stated. High-resolution mass spectra were determined on an AEI MS-902 instrument. The abbreviations used are: s, singlet; d, doublet; t, triplet; m, multiplet.

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

(20) R. E. Ireland and L. N. Mandes, *J. Org. Chem.*, **32**, 689 (1967).

(21) F. H. Howell and D. A. H. Taylor, *J. Amer. Chem. Soc.*, **80**, 1248 (1958).

ture of epimers; δ ($CDCl_3$) 5.42–4.94 (1 H, m, C*H*Br), from 1,1,4a-trimethyl-1,4,4a,-9,10,10a-hexahydro-2(3*H*)-phenanthrone.[22]

Anal. Calcd for $C_{17}H_{21}OBr$: C, 63.55; H, 6.59; Br, 24.88. Found: C, 63.75; H, 6.80; Br, 25.01.

***trans*-7-Methoxy-1,1,4a-trimethyl-4a,9,10,10a-tetrahydro-2(1*H*)-phenanthrone (19a).** A mixture of 2.64 g (7.6 mmol) of **17a** and 2.7 g of anhydrous lithium chloride in 30 ml of dry dimethylformamide was heated at reflux with stirring under nitrogen for 24 hr and then worked up to afford 2.20 g of an oil. Chromatography of this on silica gel followed by recrystallization afforded 1.10 g (50% yield) of **19a** as needles, mp 70–71° (ether–hexane). The analytical sample was prepared by sublimation; mp 72.5–73°. The crude material was satisfactory for conversion to epoxide **21a**: nmr δ ($CDCl_3$) 7.57 (1 H, d, J_{vic} = 10.5 Hz, CH=), 7.4–6.5 (3 H, m, Ar*H*), 6.00 (1 H, d, J_{vic} = 10.5 Hz, C*H*=), and 1.37, 1.22, and 1.18 (3 H each s CH_3's).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.15; H, 8.15.

Similarly prepared were **18a**, **18**, and **19**.

***trans*-7-Methoxy-4a-methyl-4a,9,10,10a-tetrahydro-2(1*H*)-phenanthrone (18a).** Reflux of a mixture of 33.0 g (0.10 mol) of **16a** and 2.9 g (0.07 g formula wt) of anhydrous lithium chloride in 300 ml of dimethylformamide for 10 hr followed by work-up as above afforded 8.3 g (34% yield) of **18a** (accompanied by 32% yield of the $\Delta^{1,10a}$ isomeric olefin, separated by chromatography): mp 140–141° (ether); nmr δ ($CDCl_3$) 7.61 (1 H, d, J_{vic} = 10.5 Hz, C*H*=), 7.5–6.5 (3 H, m, Ar*H*), 5.96 (1 H, d, J_{vic} = 10.5 Hz, C*H*=), 1.38 (3 H, s CH_3).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.33; H, 7.66.

***trans*-4a-Methyl-4a,9,10,10a-tetrahydro-2(1*H*)-phenanthrone (18).** A mixture of 500 mg (1.70 mmol) of **16** and 680 mg of calcium carbonate in 15 ml of dimethylformamide containing 3 drops of water was refluxed with stirring for 1.25 hr and worked up as above to afford 54% yield of **18**; mp 98° (hexane). The ketone was contaminated by approximately 5% of the isomeric $\Delta^{1,10a}$ ketone: nmr δ ($CDCl_3$) 7.60 (1 *H* d, J_{vic} = 10 Hz, C*H*=), 7.50–7.02 (4 H, m, Ar*H*), 5.96 (1 H, d, J_{vic} = 10 Hz, C*H*=), 1.28 (3 H, s CH_3).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.06; H, 7.72.

***trans*-1,1,4a-Trimethyl-4a,9,10,10a-tetrahydro-2(1*H*)-phenanthrone (19).** A mixture of 13.5 g of **17** and 7.0 g of anhydrous lithium chloride in 420 ml of dry dimethylformamide was refluxed with stirring for 5 hr and worked up as above to afford 7.2 g (78% yield) of **19**, as needles: mp 112° (hexane); nmr δ ($CDCl_3$) 7.61 (1 H, d, J_{vic} = 10 Hz), 7.25 (4 H, m, Ar*H*), 6.05 (1 H, d, J_{vic} = 10 Hz), and 1.42, 1.22, and 1.20 (3 H each, s CH_3's).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.81; H, 8.18.

***trans*-7-Methoxy-3a,4a-epoxy-4a-methyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (20a).** In a 3-l. three-necked round-bottomed flask equipped with a magnetic stirrer, 10- and 50-ml dropping funnels, and a nitrogen inlet tube was placed a solution of 2.111 g (0.0087 mol) of **18a** in 1500 ml of methanol. The solution was cooled to −10° in an ice–salt bath and over 6 min was added dropwise 5.0 ml (0.044 mol) of 30% hydrogen peroxide followed by 35 ml of 5% aqueous sodium hydroxide solution. The solution was stirred at −10° for 4.5 hr, 30 ml of 10% aqueous hydrochloric acid solution was added, and the reaction mixture was worked up to afford after recrystallization 2.05 g (91% yield) of **20a** as needles: mp 145–146° (ether); nmr δ ($CDCl_3$) 7.5–6.6 (3 H, m, Ar*H*), 4.07 (1 H, d, J_{vic} = 4.0 Hz, C*H*O), 3.37 (1 H, d, J_{vic} = 4.0 Hz, C*H*O), 1.15 (3 H, s, CH_3).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.95; H, 9.05.

Similarly prepared were compounds **21a**, **20**, and **21**.

***trans*-7-Methoxy-3a,4a-epoxy-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (21a)** was prepared from **19a** in 80% yield, mp 125–126° (ether–hexane).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.75. Found: C, 75.72; H, 7.56.

***trans*-3a,4a-Epoxy-4a-methyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (20)** was prepared from **18** in 60% yield, mp 95.5° (ether–hexane).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.07; H, 7.23.

***trans*-3a,4a-Epoxy-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydro-2(3*H*)-phenanthrone (21)** was prepared from **19** in 91% yield, mp 96° (hexane).

Anal. Calcd for $C_{17}H_{20}O_3$: C, 79.65; H, 7.86. Found: C, 79.40; H, 7.80.

***trans*-7-Methoxy-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydro-4a-phenanthrol (23a).** In a 100-ml three-necked round-bottomed flask equipped with a reflux condenser, two 10-ml dropping funnels, and a nitrogen inlet tube was placed a solution of 0.592 g (0.002 mol) of epoxy ketone **21a** in 40 ml of methanol under nitrogen. The solution was cooled to 0° in an ice bath and a mixture of 3.0 ml of 20.0 *N* hydrazine hydrate (0.06 mol) and 0.6 ml of glacial acetic acid was added dropwise over 5 min. The reaction was stirred at 0° for an additional 15 min, at room temperature for 15 min, heated to reflux for 13.5 hr, and then worked up to afford, on preparative tlc (Brinckmann PF-254 silica gel) 0.389 g (71% yield) of **23a**: mp 58–58.5° (ether–hexane); nmr δ ($CDCl_3$) 7.3–6.5 (3 H, m, Ar*H*), 5.80 (2 H, m, C*H*=C*H*), 4.32 (1 H, d, J_{vic} = 5 Hz, C*H*OHCH=), and 1.18, 1.10, and 1.00 (3 H each, s, $(CH_3)_2$).

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.07; H, 8.91.

Similarly prepared were compounds **22a**, **22**, and **23**.

***trans*-7-Methoxy-4a-methyl-1,4,4a,9,10,10a-hexahydro-4a-phenanthrol (22a)** was prepared from **20a** in 49% yield, an oil, purified by preparative tlc and distillation: nmr δ ($CDCl_3$) 7.4–6.5 (3 H, m, Ar*H*), 5.97 (2 H, m, C*H*=C*H*), 4.33 (1 H, broad s, $\nu - 0.5$ = 7.0 Hz, C*H*OH), 1.05 (3 H, s CH_3).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.90; H, 8.27.

***trans*-4a-Methyl-1,4,4a,9,10,10a-hexahydro-4a-phenanthrol (22)** was prepared from **20** in 55% yield, an oil purified by chromatography and distillation: nmr δ ($CDCl_3$) 7.08 (4 H, m, Ar*H*), 5.81 (2 H, m, C*H*=C*H*), 4.27 (1 H, broad s, C*H*OH). Alcohol **22** was characterized as its acetate, prepared *via* acetic anhydride–pyridine as needles, mp 71° (hexane).

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.59; H, 7.97.

***trans*-1,1,4a-Trimethyl-1,4,4a,9,10,10a-hexahydro-4a-phenanthrol (23)** was prepared from **21** in 38% yield as needles: mp 73–75° (hexane); nmr δ ($CDCl_3$) 7.10 (4 H, m, Ar*H*), 5.85 (1 H, double d, J_a = 10 Hz, J_b = 5 Hz CH=C*H*—CHOH), 5.63 (1 H, d, J_{vic} = 10 Hz, C*H*=CHCHOH), 4.41 (1 H, d, J_{vic} = 5 Hz, CH=CHC*H*OH), and 1.18, 1.10, and 0.99 (3 H each, s, CH_3's).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.34; H, 9.30.

6-Methoxy-2-formyl-2-(pentan-3′-one)-1-tetralone (24). A mixture of 2.00 g (0.012 mol) of 2-hydroxymethylene-6-methoxy-1-tetralone,[23] 1.45 g (0.017 mol) of 1-pentene-3-one, and 5 drops of triethylamine was allowed to stand under nitrogen at room temperature for 3 days. The reaction mixture was taken up in 200 ml of ether and was washed successively with 2 *N* aqueous sodium carbonate solution, saturated salt solution, was dried over magnesium sulfate, and was concentrated *in vacuo* to afford 2.40 g of an oil. The material was further purified by preparative tlc: δ ($CDCl_3$) 9.62 (1 H, s C*H*=O), 8.02, 7.0–6.6 (1 H, 2 H, m, Ar*H*) 3.85 (3 H, s, OCH_3), 3.00 (2 H, t, J_{vic} = 7 Hz, $COCH_2$), 2.7–1.7 (8 H, m), 1.03 (3 H, t, J_{vic} = 7 Hz, $COCH_2$), 2.7–1.7 (8 H, m), 1.03 (3 H, t, J_{vic} = 7 Hz, CH_2CH_2CO); $\nu_{max}^{CHCl_3}$ 5.88, 6.01 μ.

Reflux of **24** in 1% aqueous methanolic (1:1) potassium hydroxide afforded not deformylated products but primarily (60% yield) spiroendione **25**: mp 133–134° (ether); δ ($CDCl_3$) 7.95, 7.0–6.6 (3 H, m, Ar*H*), 6.48 (1 H, s, $\nu - 0.5$ = 3.5 Hz, C*H*=C), 1.80 (3 H, d, *J* = 1.5 Hz, CH_3=CH); *m/e* 270 (parent), 242 (P − 28), 148 (base).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.75; H, 6.83.

6-Methoxy-2-(pentan-3′-one)-1-tetralone (26). A mixture of 444 mg (1.54 mmol) of **24** and 21 mg of potassium carbonate in 10 ml of ethanol and 0.2 ml of water was heated under reflux for 24 hr, cooled, and worked up to afford 310 mg (77% yield) of **26**; mp 86–86.5° (ether); *m/e* 260 (parent).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.90; H, 7.59.

A mixture of 1.39 g (5.4 mmol) of **26** and 1.68 g of potassium hydroxide, 50 ml of water, and 150 ml of methanol was refluxed for

(22) J. Delobelle and M. Fetizon, *Bull. Soc. Chim. Fr.*, 1632 (1961).

(23) A. A. Akrem and I. G. Zavelskaya, *Izv. Akad. Nauk, Otd. Khim. Nauk*, **9**, 1637 (1960).

10 hr, cooled, and worked up to afford 777 mg (60% yield) of **27**, mp 77–77.5 (ether–hexane).

Anal. Calcd for $C_{26}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.14; H, 7.38.

7-Methoxy-4-methyl-1,2,9,10,10a-hexahydrophenanthrene (11a). To a mixture of 0.43 g of anhydrous aluminum chloride and 61 mg of lithium aluminum chloride in 10 ml of ether was added dropwise a solution of 200 mg (0.81 mmol) of **27** in 5 ml of ether. The mixture was refluxed for 30 min, excess reducing agent was destroyed by addition of dilute sulfuric acid, and the reaction mixture was worked up to afford, after preparative tlc and molecular distillation 128 mg of **11a** as an oil, homogeneous by glc: λ_{max}^{EtOH} 258 (13,200).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83; *m/e* 228.1514. Found: C, 84.25; H, 8.60; *m/e* 228.1524.

7-Methoxy-4-methyl-1,2,3,4-tetrahydro-4-phenanthrol. Reaction of ketone **28**[24] with methylmagnesium iodide (from 0.71 g of methyl iodide) followed by aqueous ammonium chloride work-up afforded 403 mg (76% yield) of the title compound as needles, mp 128–129° (ether).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.44; H, 7.39.

7-Methoxy-4-methyl-1,2-dihydrophenanthrene was isolated as needles, mp 71–72° (ether) in 30% yield (100% yield of crude olefin), on refluxing a solution of the above alcohol and *p*-toluenesulfonic acid in benzene.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19; *m/e* 224.1201. Found: C, 85.95; H, 7.28; *m/e* 224.1208.

7-Methoxy-4-methylphenanthrene. A mixture of 608 mg (2.65 mmol) of the above olefin and 1.14 g (5.0 mmol) of 2,3-dichloro-5,6-dicyanoquinone in 25 ml of dry benzene was refluxed for 1 hr, cooled, filtered, and worked up to afford 400 mg of an oil on molecular distillation. Crystallization of this from hexane afforded 150 mg of the phenanthrene as plates, mp 37–38°. Its nmr spectrum exhibited 3 H singlets at δ 3.97 and 3.12.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.53. Found: C, 86.41; H, 6.28.

***trans*-7-Methoxy-1,1,4a-trimethyl-1,2,4a,9,10,10a-hexahydrophenanthrene (12a).** A mixture of 46 mg (0.13 mmol) of **2a** and 40 mg of potassium *tert*-butoxide in 2 ml of dry 1,2-dimethoxyethane was refluxed with stirring under nitrogen for 2 hr, cooled, and worked up to afford 30 mg (91% yield) of an oil. Preparative tlc followed by molecular distillation of this afforded 25 mg (76% yield) of **12a**, an oil: δ ($CDCl_3$) 6.3 (1 H, m, C*H*=), 5.7 (1 H, m, C*H*=), δ 1.20, 0.98 (3 H, 6 H, s, C*H*$_3$'s); *m/e* 256.1825 (calcd for $C_{18}H_{24}O$: 256.1827).

Similarly prepared were compounds **8a**, **8**, and **12**.

***trans*-7-Methoxy-4a-methyl-1,2,4a,9,10,10a-hexahydrophenanthrene (8a)** was isolated in 83% yield from **1a** as an oil, homogeneous by glc: *m/e* 228.1524 (calcd for $C_{16}H_{20}O$: 228.1514).

4a-Methyl-1,2,4a,9,10,10a-hexahydrophenanthrene (8) was isolated in 62% yield from **1** as an oil: *m/e* 198.1411 (calcd for $C_{15}H_{18}$: 198.1409).

1,1,4a-Trimethyl-1,2,4a,9,10,10a-hexahydrophenanthrene (12) was isolated in 60% yield from **2** as an oil: *m/e* 226.1727 (calcd for $C_{17}H_{22}$: 226.1722).

***trans*-8-Methoxy-4a-methyl-1,2,3,9,10,10a-hexahydro-4(4a*H*)-phenanthrone (29a).** A solution of 102 mg (0.414 mmol) of **4a** in 5 ml of acetone was oxidized by Jones' reagent[25] to afford on work-up and preparative tlc 87 mg (86% yield) of **29a**: an oil; *m/e* 244.1471 (calcd for $C_{16}H_{20}O_2$: 244.1463); δ ($CDCl_3$) 7.4–5.5 (3 H, m, Ar*H*), 1.45 (3 H, s, C*H*$_3$); $\lambda_{max}^{CHCl_3}$ 5.87 μ.

Similarly prepared from **4** was ***trans*-4a-methyl-1,2,3,9,10,10a-hexahydro-4(4a*H*)-phenanthrone (29)**, an oil purified by chromatography followed by molecular distillation: $\nu_{max}^{CHCl_3}$ 5.88 μ; *m/e* 214 (parent). Its 2,4-dinitrophenylhydrazone, red needles, had mp 233–235° dec.

***trans*-7-Methoxy-4a-methyl-1,2,3,4,4a,9,10,10a-octahydro-4β-phenanthrol (6a).** A mixture of 87 mg (0.36 mmol) of **29a** and 1.844 g (10 mmol) of aluminum isopropoxide in 50 ml of anhydrous isopropyl alcohol under nitrogen was boiled for 48 hr. Distillate, 7 ml per hr, was removed (spinning band column) and alcohol was added periodically to keep the reaction volume constant. The mixture was cooled and worked up to afford after preparative tlc 57 mg (65% yield) of **6a**, an oil: δ ($CDCl_3$) 8.22 (1 H, broad d, Ar*H*$_5$), 6.9–6.5 (2 H, m, Ar*H*$_6$ and Ar*H*$_8$).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.12; H, 8.92.

Its methanesulfonate, **3a**, was prepared as above and isolated in 97% yield as an oil: δ ($CDCl_3$) 7.80, 6.9–6.5 (1 H, 2 H, m, Ar*H*), 4.75 (1 H, double d, J_{ax} = 10.5 Hz, J_{eq} = 4 Hz, C*H*OSO$_2$-CH$_3$), 1.27 (3 H, s, C*H*$_3$).

Anal. Calcd for $C_{17}H_{24}O_4S$: C, 6.294; H, 7.46; S, 9.88. Found: C, 63.18; H, 7.45; S, 9.72.

Similarly, ***trans*-4a-methyl-1,2,3,4,4a,9a,10,10a-octahydro-4β-phenanthrol (6)** was prepared by aluminum isopropoxide reduction of **29**. It was isolated in 70% yield as an oil, contaminated with ~3% of **4**. Its nmr spectrum exhibited δ ($CDCl_3$) 3.91 (1 H, double d, J_{ax} = 10 Hz, J_{eq} = 5 Hz, C*H*OH). It was characterized as its methanesulfonate **1**, prepared as above in 68% yield as needles: mp 71° dec (ether–hexane); δ ($CDCl_3$) 4.80 (1 H, double d, J_{ax} = 10 Hz, J_{eq} = 5 Hz, C*H*OSO$_2$CH$_3$).

Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.29; H, 7.53; S, 10.87. Found: C, 65.07; H, 7.58; S, 10.82.

For preparative acetolysis alcohols **6** and **6a** were purified by preparative glc from their epimers **4** and **4a**.

***trans*-7-Methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydro-4a-phenanthrol (5a) and Its Methanesulfonate 2a.** A mixture of 82 mg (0.30 mmol) of **23a** and 100 mg of 10% palladium on charcoal in 10 ml of 95% ethanol containing 1 drop of 10% alcoholic potassium hydroxide absorbed 6.8 ml of hydrogen (at 1 atm) over 24 hr. The mixture was filtered and worked up to afford 77 mg (94% yield) of **5a** as needles: mp 82.5–83° (ether–hexane); nmr δ 4.93 (1 H, s, ν − 0.5 = 60 Hz, C*H*OH).

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 79.02; H, 9.72.

To a solution of 55 mg (0.20 mmol) of **5a** in 0.5 ml of pyridine at 0° was added 0.021 ml (0.26 mmol) of distilled methane sulfonyl chloride. The solution was allowed to stand at 7° for 24 hr and worked up to afford 60 mg (86% yield) of **2a** as rhombs: mp 90–91° (ether–hexane); nmr δ ($CDCl_3$) 5.43 (1 H, s, ν − 0.5 = 7.0 Hz, C*H*OSO$_2$CH$_3$).

Anal. Calcd for $C_{19}H_{28}O_4S$: C, 67.47; H, 8.01; S, 9.10. Found: C, 64.59; H, 8.02; S, 9.15.

Similarly prepared were compounds **4a**, **4**, and **5**.

***trans*-7-Methoxy-4a-methyl-1,2,3,4a,9,10,10a-octahydro-4a-phenanthrol (4a)** was prepared from **22a** and 10% palladium on charcoal in ethyl acetate, as needles: mp 73.5–74° (ether–hexane); nmr δ ($CDCl_3$) 4.32 (1 H, s, ν − 0.5 = 5.0 Hz, C*H*OH).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.95; H, 9.05.

Its methanesulfonate, **1a**, was prepared as above and isolated as rhombs: mp 76.5–77° (ether–hexane); nmr δ ($CDCl_3$) 5.42 (1 H, s, ν − 0.5 ~ 6 Hz, C*H*OSO$_2$CH$_3$).

Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.94; H, 7.46; S, 9.88. Found: C, 62.70; H, 7.23; S, 10.01.

***trans*-4a-Methyl-1,2,3,4,4a,9,10,10a-octahydro-4-phenanthrol (4)** was prepared in 80% yield from **22** and 30% palladium on charcoal in cyclohexane: needles, mp 73° (ethanol–water); nmr δ ($CDCl_3$) 4.34 (1 H, s, ν − 0.5 = 5 Hz, C*H*OH); mass spectrum *m/e* 216 (parent). Its methanesulfonate, **1**, was prepared as above in 77% yield as needles: mp 100–101° dec; nmr δ ($CDCl_3$) 5.43 (1 H, s, ν − 0.5 = 6 Hz, C*H*OSO$_2$CH$_3$).

Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.29; H, 7.53; S, 10.87. Found: C, 65.58; H, 7.67; S, 10.76.

***trans*-1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydro-4-phenanthrol (5)** was prepared from **23** and 30% palladium on charcoal in ethanol in 92% yield, as needles: mp 91–92°; nmr δ ($CDCl_3$) 4.41 (1 H, s, ν ~ 6 Hz, C*H*OH).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.54: H, 9.91. Found: C, 83.51; H, 9.98.

Its methanesulfonate, **2**, was prepared as above as unstable needles, mp 94° dec (ether–hexane).

Acetolysis of Methanesulfonate 1. A mixture of 50 mg (0.17 mmol) of **1** and 170 mg (2.57 mg formula wt) of anhydrous sodium acetate in 20 ml of anhydrous acetic acid was heated under reflux with stirring under nitrogen for 2 hr. The cooled reaction mixture was partitioned between water and ether and the combined ether layers were washed with saturated sodium bicarbonate solution, water, and saturated salt solution, dried ($MgSO_4$), and evaporated. The residual oil (62 mg) was dissolved in 7:3 hexane–benzene and passed through a Florisil column to afford on evaporation 36 mg (95% yield) of a clear oil. The infrared spectrum of the oil had no appreciable absorption maxima on the 5.6–5.9-μ region: nmr δ

(24) A gift from Professor A. L. Wilds.

(25) A. Bowers, T. C. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

($CDCl_3$) 7.24 (4 H, m, Ar*H*), 3.01–2.60 (3 H, broad band), 2.31–1.22 (8 *H*, broad band), 1.10 (3 H, d, J_{vic} = 7 Hz, CH_3CH); *m/e* 198.1411 (calcd for $C_{15}H_{18}$: 198.1409); λ_{max}^{EtOH} 265 mμ (10,500).

Analytical glc (150-ft Apiezon L capillary column, 184°) indicated the product to be a mixture of seven components: A (identified as **7** by aromatization (see below)), 91.9% B, identified by cochromatography with an authentic sample as **8**, 4.8%; C, identified as **9**, the major product from acetolysis of **3**, by cochromatography, 0.9%; and D–G, all unidentified, in 0.7, 0.4, 0.9, and 0.4%, respectively.

A mixture of 26 mg of the acetolysis olefin mixture and 270 mg of 2,3-dichloro-5,6-dicyanoquinone in 2 ml of chlorobenzene was heated under reflux for 1 hr, cooled, filtered, and worked up. The resulting oil, 14 mg, was separated by preparative glc into two fractions in a 1:3 proportion: phenanthrene, identified by comparison with an authentic sample, and 4-methylphenanthrene, identified by comparison (ir, mp 49°, mmp 49°, lit.[26] mp 49–50°, glc) with a sample synthesized according to Bachman and Edgerton.[26]

Acetolysis of 1a. A mixture of 72 mg (0.222 mmol) of **1a** and 182 mg of anhydrous sodium acetate in 75 ml of anhydrous acetic acid was heated under reflux, with stirring under nitrogen, for 3 hr, cooled, and partitioned between water and ether. The combined ether extracts were washed as above, dried, and evaporated to afford 51 mg (100% yield of yellowish crystals). Analytical glc of the crude material indicated it to be a 2.3:97.7 mixture. The 2.3% component was identified as **8a** by cochromatography with an authentic sample. Recrystallization (ether–hexane) afforded the major component (**7a**) as needles: mp 52.5–53°; λ_{max}^{EtOH} 270 mμ (13,800); δ (100 MHz, $CDCl_3$) 9.2–6.6 (3 H, m, Ar*H*), 3.76 (3 H, s, $CO\mathit{H}_3$), 2.85 (1 H, broad, $C\mathit{H}CH_3$ (confirmed by spin decoupling), 2.70–2.56 (2 H, broad, $C\mathit{H}$—C=C), 2.4–1.4 (8 H, broad band)), 1.08 (3 H, d, J_{vic} = 6.7 Hz, $C\mathit{H}_3CH$ (confirmed by decoupling)).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83; *m/e* 228.1515. Found: C, 84.32; H, 8.64; *m/e* 228.1524.

Aromatization of 7-Methoxy-4-methyl-1,2,3,4,9,10-hexahydrophenanthrene (7a). A mixture of 80 mg of **7a** and 800 mg of 2,3-dichloro-5,6-dicyanoquinone in 15 ml of benzene was heated under reflux for 3.5 hr, cooled, and worked up to afford, on preparative tlc and glc, 16 mg of 2-methoxy-5-methyl phenanthrene, identified by comparison (glc, ir, nmr) with a sample synthesized as above.

Acetolysis of 3. A mixture of 75 mg (0.255 mmol) of **3** and 75 mg (0.916 mmol) of anhydrous sodium acetate in 35 ml of anhydrous acetic acid was heated under reflux with stirring under nitrogen for 2 hr, cooled, and worked up as above to afford 46 mg (91% yield) of an oil. Both nmr and ir indicated the absence of acetates. Analytical glc gave the following composition: A, 3.9%, identified as **7** by cochromatography with an authentic sample; B, 0.8%, identified as **8** by cochromatography with an authentic sample; C, 81.8%, identified below as **9**; and D–H, all unidentified in 10.6, 0.2, 0.4, 1.9, and 0.6%, respectively. Preparative glc afforded olefin C (**9**) in 95% purity: δ ($CDCl_3$) 7.2 (4 H, m, Ar*H*), 2.82–2.17 (5 H, broad band, $C\mathit{H}$—C=C), 2.07 (3 H, s, $C\mathit{H}_3C$=), 1.95–1.16 (6 H, broad); *m/e* 198.3194 (calcd for $C_{15}H_{18}$: 198.1409), 183 (P − CH_3, base); λ_{max}^{EtOH} 258 (7900).

Hydroxylation of **9** was accomplished by allowing a mixture of 46 mg of crude C, 60 mg of osmium tetroxide, 0.10 ml of pyridine, and 4 ml of dry ether to stand at room temperature for 24 hr. To the mixture was then added mannitol (150 mg) and 1.5 ml of 10% aqueous sodium hydroxide. The resulting black mixture was stirred for 20 hr at room temperature, diluted with water, and extracted with ether. The combined ethereal extracts were washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, water, and brine.

After drying (magnesium sulfate) the solvent was removed to afford crude crystalline *vic*-diol **30** (49 mg, 90% yield): δ ($CDCl_3$) 1.45 (3 H, s, $C\mathit{H}_3$). The crude diol (47 g) was allowed to react with a solution of potassium penodate (49 mg) in 3.5 ml of 1 *N* sulfuric acid at room temperature under nitrogen. After stirring for 64 hr the reaction mixture was diluted with water and extracted with ether. The combined ethereal extracts were washed with saturated sodium bicarbonate solution, water, and saturated salt solution, and evaporated to afford, on preparative tlc (Brinkmann PF-254 silica gel, 7.3 benzene–ethyl acetate), 9 mg (19% yield from crude C) of a homogeneous (tlc) oil (**31**): $\lambda_{max}^{CHCl_3}$ 5.78, 5.95 μ; *m/e* 230 (base, 1%), 215 (P − 15, 26%), 187 (P − 43, 12%), 146 (P − 84, 60%), 131 (P − 99, 54%), and 91 (P − 139, base).

Acetolysis of equatorial methanesulfonate **3a** proceeded in a similar manner to afford a 91% yield of an oily olefin mixture which analytical glc indicated to contain three components: A, 94%; B, ~0.2%; C, ~0.2%; and D, ~5.7%. The nmr spectrum of A (**9a**) was essentially superimposable on that of **9** except for the presence of a peak at δ 3.78 ($OC\mathit{H}_3$) in the former: uv λ_{max}^{EtOH} 254 (9430); mass spectrum *m/e* 228.1524 (calcd for $C_{16}H_{24}O$: 228.1515). By cochromatography C was identified as **8a** and D was identified as **7a**.

Acetolysis of Methanesulfonate 2. A mixture of 161 mg (0.497 mmol) of **2** and 50 mg of anhydrous sodium acetate in 50 ml of dry acetic acid was refluxed for 2 hr, cooled, and worked up as above to afford 110 mg of a clear oil whose ir was devoid of peaks assignable to the acetate group. Analytical glc indicated it to be a mixture of three components: A, 80%; B, 17%; and C, 3%. The mass spectrum of the mixture exhibited a parent peak at *m/e* 226.1727 ($C_{17}H_{22}$ requires 226.1722) with a base peak at *m/e* 211 (P − CH_3). The uv (λ_{max}^{EtOH} 262 (10,800)) is primarily ascribable to A. The fraction C cochromatographed with the elimination product **12**.

A mixture of 110 mg of the above olefin mixture and 131 mg of 2,3-dichloro-5,6-dicyanoquinone in 5 ml of benzene was stirred at room temperature for 8 hr, filtered, and worked up to afford 90 mg of a yellow oil. Preparative glc of this (5 ft × 1/2 in. 20% Carbowax, 220°) followed by molecular distillation of the major peak afforded 33 mg (30% yield) of **13**, an oil, homogeneous by glc: δ (CCl_4) 7 (6 H, broad band, Ar*H*), 1.40 (3 H, s, $C\mathit{H}_3$), 1.37 (3 H, d, J_{vic} = 7.0 Hz, $C\mathit{H}_3CH$), 1.26 (3 H, s, $C\mathit{H}_3$); λ_{max}^{EtOH} 290 (4500, sh), 280 (6150), 272 (6050), 228 mμ (93,000); *m/e* 224.1565 ($C_{17}H_{20}$ requires 224.1581) (26%), 209 (base, P − CH_3), 194 (7% P − 30), 179 (20% P − 45).

Acetolysis of methanesulfonate **2a** in the same fashion afforded a quantitative yield of nonacetate-containing products having the constitution A, 88% B, 9%, and C, 3% by analytical glc. Olefin C cochromatographed with **12a**, B was unidentified, and A was identified as **10a** by the spectral properties of a pure sample obtained by preparative glc and by partial aromatization: uv λ_{max}^{EtOH} 267 (17,000); nmr δ (C_6H_6, 100 MHz) 3.39 (3 H, s, $OC\mathit{H}_3$), 2.75 (1 H, broad s, ν − 0.5 = 18 Hz, $C\mathit{H}CH_3$ (confirmed by decoupling)), 1.13 (3 H, d, J_{vic} = 6.8 Hz $C\mathit{H}_3CH$ (confirmed by decoupling)), and 1.09 and 0.95 (3 H each, s, $C\mathit{H}_3$); mass spectrum *m/e* 256.1825 ($C_{18}H_{24}O$ requires 256.1827), 241 (P − 15, base).

A mixture of 95 mg of the acetolysis olefin mixture and 102 mg of 2,3-dichloro-5,6-dicyanoquinone in 4 ml of benzene was stirred at 25° for 19 hr and worked up to afford 79 mg of an oil. Preparative glc of this with collection of the major (97%) peak afforded 75 mg (80% yield) of a homogeneous (glc) oil assigned structure **13a**: λ_{max}^{EtOH} 227 (33,800), 232 (32,500), 255 (3270, sh), 264 (4270), 274 (4450), 283 (3180, sh), 305 (817), 318 (1090), 326 (999), and 333 (1450); δ ($CDCl_3$) 8.2–6.5 (5 H, m, Ar*H*) 4.2–3.3 (1 H, broad band $C\mathit{H}CH_3$ (confirmed by decoupling)), 3.85 (3 H, s, $OC\mathit{H}_3$), 1.35 (3 *H*, d, J_{vic} = 7 Hz, $C\mathit{H}_3CH$ (confirmed by decoupling)), and 1.38 and 1.25 (3 H each, s, $C\mathit{H}_3$'s); *m/e* 256 (P, 37%), 249 (P − 15, base).

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72; *m/e* 254.1671. Found: C, 84.69; H, 9.00; *m/e* 254.1678.

Kinetic Analysis of Acetolyses. The acetolysis reactions were followed by sealing 1-ml aliquots of a solution of the methanesulfonate ester (~15 mg) in 25 ml of anhydrous acetic acid containing anhydrous sodium acetate (~15–25 mg) into 2-ml ampoules. The ampoules were immersed in a constant temperature bath. At intervals an ampoule was removed and quickly chilled to 0°, opened, and diluted to 10 ml with 95% ethanol, and an ultraviolet spectrum (Cary Model 15) of the resulting solution was determined. A convention at least-squares plot of log X_0/X, where $X = (OD - OD_t)/(OD - OD_0)$ and OD_r = the optical density of the solution at a chosen wavelength (the absorption maxima of the developing styrene chromopore) at time *t*, *vs.* time affords the first-order rate constant and error. Infinity OD points, ~20 half-lives, were stable. The results are presented in Table II.

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(26) W. E. Bachmann and R. O. Edgerton, *J. Amer. Chem. Soc.*, **62**, 2219 (1940).