The ultraviolet spectrum exhibited $\lambda_{\max}^{C_2H_5OH}$ 242 mμ (ε 3590) and indicated that 16.7% of a conjugated diene was present.[17]

Quantitative hydrogenation at atmospheric pressure of a sample of the product in 95% ethanol over 10% palladium on charcoal showed a total diene content of 16.7%.

2,5-Diethyl-2,5-dimethyltetrahydrofuran (V).—A mixture of 8.5 g. (0.048 mole) of 3,6-dimethyl-3,6-octanediol (from Air Reduction Chemical Co.) and 45.5 g. (0.58 mole) of dimethyl sulfoxide was heated for 17.5 hr. at 170°. Water was added to the cooled reaction mixture which was then extracted with two 100-ml. portions of petroleum ether. The combined petroleum ether extracts were concentrated after drying over calcium sulfate. Distillation of the remaining liquid furnished 4.85 g. (70%) of product, b.p. 161–163°, n^{25}D 1.4378 (reported[2c] b.p. 162–165°, $n^{13.6}$D 1.4300). The infrared spectrum showed no trace of OH absorption and a very small peak at 6.0 μ (C=C). The characteristic band of cyclic ethers was present at 9.23 μ.

Gas chromatographic analysis of the product gave five peaks with the composition of 61.4%, 24.7%, 5.5%, 4.7%, and 3.6%, respectively, as determined by the peak area method.[18]

This liquid exhibited an ultraviolet spectrum $\lambda_{\max}^{C_2H_5OH}$ 239 mμ (ε 3470) and $\lambda_{\max}^{C_2H_5OH}$ 245 mμ (ε 3620).

Quantitative hydrogenation of a sample at atmospheric pressure in ethanol over 10% palladium-on-charcoal catalyst gave total diene content of 15.05%.

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[17] Pure 2,5 dimethyl 2,4-hexadiene exhibits $\lambda_{\max}^{C_2H_5OH}$ 242 mμ (ε 21,500). E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1425 (1952).

[18] Retention times of the peaks were 9.9, 11.0, 11.8, 13.1, and 14.0 min., respectively. Flow rates of helium was 42.5 ml./min. with a detector temperature of 132° and column temperature 122°.

Steroids. CCXXXII.[1] One-step Rearrangement of 17α-Methyl-$\Delta^{1,4,6}$-androstatrien-17-ol-3-one to an 18-Norequilenin Derivative

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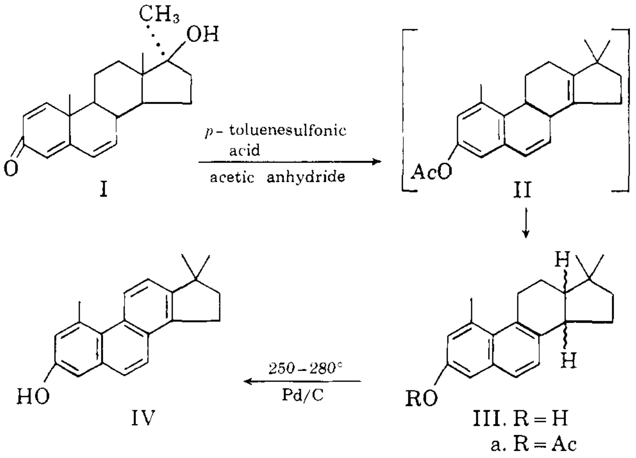
Some time ago it was reported from these laboratories that the dienone–phenol rearrangement of $\Delta^{1,4,6}$-androstatrien-3-one derivatives leads to 1-methyl-Δ^6-estrogens.[2] We have now found that under the conditions used previously (heating with *p*-toluenesulfonic acid in acetic anhydride) 17α-methyl-$\Delta^{1,6,4}$-androstatrien-17-ol-3-one (I)[3] undergoes simultaneously a Wagner–Meerwein rearrangment of the 17-hydroxy and 13-methyl groups, dehydration and migration of the Δ^{13} double bond into ring B. Alkaline hydrolysis led to a crystalline substance (over-all yield, 21%), to which structure III (3′,3′,5-trimethyl-7-hydroxy-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene) has been assigned, based on the following considerations.

Tortorella, *et al.*,[4] have shown that the Wagner–Meerwein reaction of 17α-methyl-Δ^5-androstene-3β-17-diol and of 17α-methylandrostane-3β-17-diol gives rise to a double bond in position 13. The migration of the latter into ring B is facilitated by the presence of the Δ^6 double bond in an intermediate such as II. Structure III is confirmed by the ultraviolet spectrum (Fig. 1), which is similar to that of 1-methyldihydroequilenin,[2] as well as by the infrared and n.m.r. spectra.[5] In the latter the 17-*gem*-dimethyl group appears as two 3-proton singlets at 53.3 and 64.5 c.p.s., and the protons of the methyl of the aromatic ring resonate at 119.7 c.p.s. (singlet). Two broad unresolved multiplets equivalent, respectively, to two and one protons, are due to the benzylic protons at C-11 (*ca.* 209 c.p.s.) and at C-14 (*ca.* 255 c.p.s.). The aromatic protons at C-2 and C-4 both resonate close to 409 c.p.s., so that a broadened single peak is observed. Mutual long-range coupling between these two protons and between those at C-4 and C-6 may also be responsible for the broadening of this absorption. A typical AB quartet at 422.8, 431.3, 438.0, and 446.5 c.p.s. (J = 8.5 c.p.s.) appears for the adjacent protons at C-6 and C-7.



Substance III contains two asymmetric centers at C-13 and C-14, which, though present in the starting material I, had been destroyed in the intermediate Δ^{13}-compound (*e.g.*, II). That no racemization had occurred was shown by the fact that III was optically active ([α] D + 43.5°). The stereochemistry of II was not established but we believe the substance to possess the thermodynamically more stable *cis* C/D-ring junction.[6]

The acetate of compound III is easily dehydrogenated with palladium–carbon at 250–280°. Subsequent alkaline hydrolysis yielded the fully aromatic optically inactive 3′,3′,5-trimethyl-7-hydroxy-1,2-cyclopentenophenanthrene (IV).

Experimental[7]

3′,3′,5-Trimethyl-7-hydroxy-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene (III).—A solution of 10 g. of 17α-methyl-$\Delta^{1,4,6}$-androstatrien-17-ol-3-one (I)[3] in 150 ml. of acetic anhydride containing 3 g. of *p*-toluenesulfonic acid was heated on the steam bath for 5 hr. The solution after cooling was poured into 2 l. of water and the mixture was allowed to stand overnight. The oily precipitate was extracted with ether. The extract, after being washed with water and sodium bicarbonate solution,

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[1] Paper CCXXXI. O. Halpern, R. Villotti, and A. Bowers, *Chem. Ind.* (London), in press.

[2] C. Djerassi, G. Rosenkranz, J. Romo, J. Pataki, and S. Kaufmann, *J. Am. Chem. Soc.*, **72**, 4540 (1950).

[3] British Patent 854,343.

[4] V. Tortorella, G. Lucente, and A. Romeo, *Ann. chim.* (Rome), **50**, 1198 (1960).

[5] We are indebted to Dr. Alexander Cross for the n.m.r. measurement and interpretations. The n.m.r. spectrum was taken with a *ca.* 5% solution in deuteriochloroform containing tetramethylsilane as an internal reference standard. A Varian A-60 spectrometer was used. Chemical shifts are presented as c.p.s. from the reference and are accurate to ±1 c.p.s. Coupling constants, J, are also expressed as c.p.s. and are accurate to ±0.5 c.p.s.

[6] *Cf.* L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Co., New York, N. Y., 1959, pp. 461, 464.

[7] Melting points were determined in a Thomas-Hoover melting point apparatus and rotations have been recorded in chloroform. We are indebted to Dr. Claudio Zapata and his staff for the determination of all rotations and the recording of spectra.

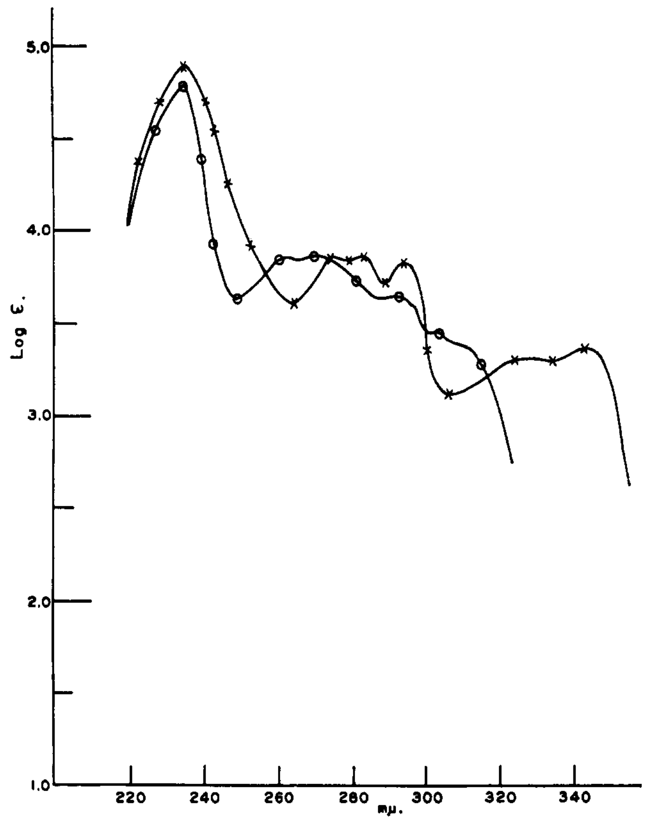

Fig. 1.—Ultraviolet absorption spectra: III ○—○—○; 1-methyl-17-dihydroequilenin, x—x—x.

was dried with anhydrous sodium sulfate and evaporated to dryness. The oily residue was dissolved in 200 ml. of methanol and a solution of 10 g. of sodium hydroxide in 20 ml. of water was added. The solution was refluxed for 1 hr., when 2 l. of water was added and the mixture was acidified with 2 *N* hydrochloric acid. After being collected, the resulting amorphous precipitate was dissolved in ether, dried, and treated with 1 g. of activated charcoal. The decolorized solution was concentrated to small volume and hexane was added when crystallization of fine needles started. Several recrystallizations from ether hexane yielded 2.1 g. (21%) of pure III, m.p. 163.5–164°, $[\alpha]_D$ +43.5°, λ_{max}^{MeOH} 235, 261, 270, 282, 293, and 314 mμ, log ε 4.78, 3.83, 3.84, 3.74, 3.63, and 3.28, respectively; λ_{max}^{KBr} 3.14, 6.19, 7.39, and 7.91 μ.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.71; H, 8.57. Found: C, 86.06; H, 8.44.

Acetate (IIIa).—The acetate of compound III was prepared with acetic anhydride and pyridine at room temperature.

It crystallized from methanol as plates, m.p. 82–83.5°, $[\alpha]_D$ + 45.9°, λ_{max}^{MeOH} 235, 263, 270, 284, 315 and 325 mμ, log ε 4.84, 3.83, 3.68, 3.76, 3.31, and 3.31, respectively; λ_{max}^{KBr} 2.94, 3.44, 5.69, 7.29, and 8.09μ.

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 81.94; H, 8.13. Found: C, 82.05; H, 8.23.

3′,3′,5-Trimethyl-7-hydroxy-1,2-cyclopentenophenanthrene (IV).—A mixture of 2.5 g. of IIIa and 2 g. of 5% palladium–carbon was heated in an oil bath at 250–280° for 4 hr. The cooled reaction product was diluted with ether and the catalyst was removed by filtration. The filtrate was evaporated to dryness and the residual oil was saponified by being boiled for 1 hr. with a solution of 2 g. of sodium hydroxide in 5 ml. of water and 50 ml. of methanol. The reaction mixture was poured into 1 l. of water, acidified with 2 *N* hydrochloric acid, and extracted several times with ether. The combined extracts were washed with water and sodium bicarbonate solution, and then dried with anhydrous sodium sulfate. After concentration to a small volume, compound IV was precipitated with hexane. Two crystallizations from ether–hexane yielded 1 g. of pure product m.p. 144–145°, $[\alpha]_D$ 0, λ_{max}^{MeOH} 227, 262, 284, 296, and 307 mμ, log ε 4.23, 4.82, 4.13, 4.03, and 4.05, respectively.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.91; H, 7.29. Found: C, 86.57; H, 7.22.

Rearrangement of 2-Cyano-3-*t*-butyl-1-indenone

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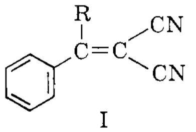
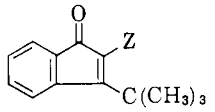
The formation of substituted indenones and indanones from the acid treatment of α-cyano-β-substituted cinnamonitriles I has been reported.[2] It was shown that, when the R groups in I were CH_3, C_2H_5, *i*-C_3H_7, or C_6H_5, cyclic ketoamides are produced, but that ring closure of I (R = *t*-C_4H_9) furnishes the cyano ketone IIa. Since the ketoamide IIb was desired, especially for ultraviolet study, several attempts to prepare it by hydration of IIa were made. Under several different acid conditions, the ketoamide was not formed; instead, a nitrile isomeric with IIa, as indicated by its elemental analysis and molecular weight determination, was isolated.



I

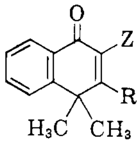


IIa. Z = CN
b. Z = CONH₂

Compound IIa is a yellow solid, m.p. 198°, while the isomer is white, and melted at 165°. In contrast to the infrared spectrum of IIa, which possessed peaks at 2252 cm.$^{-1}$ (CN) and 1720 cm.$^{-1}$ (CO), the spectrum of the white compound had a peak at 2250 cm.$^{-1}$ (CN), but the carbonyl vibrational frequency had been shifted to 1662 cm.$^{-1}$. A change in the ultraviolet spectrum was also observed. The spectrum of the white compound displayed a λ_{max} at 251 mμ (ε 19,300), as compared with λ_{max} 244 mμ (ε 35,000) for IIa.

Josier and Fuson[3] report that substituted 1-indenones show carbonyl absorption in the region of 1710–1740 cm.$^{-1}$ and α,β-unsaturated six-membered cyclic ketones near 1665 cm.$^{-1}$. Hassner and Cromwell[4] have found that 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IIIa) and 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IIIb) have peaks in the infrared at 1665 cm.$^{-1}$ and 1662 cm.$^{-1}$, and λ_{max} values in the ultraviolet at 242 mμ (ε 10,600) and 252 mμ (ε 11,000), respectively.

The evidence presented thus far suggests a rearrangement of IIa involving ring expansion to 2-cyano-3,4,4-



III

a. R = Z = H
b. R = H, Z = $CH_2C_6H_5$
c. R = CH_3, Z = CN
d. R = CH_3, Z = $CONH_2$

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[1] Contribution no. 1105, taken in part from a thesis submitted to Indiana University in partial fulfillment of the requirements for the degree Doctor of Philosophy, June, 1962, by D. M., Bristol Predoctoral Fellow, 1960–1962.

[2] E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and Donald R. Maulding, *J. Org. Chem.*, **27**, 4428 (1962).

[3] M. L. Josier and N. Fuson, *Bull. soc. chim. France*, 389 (1952).

[4] A. Hassner and N. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).