

**1048.** *Spectra and Stereochemistry. Part VI.<sup>1</sup> A Novel Cleavage of Ring D during Dehydrogenation of Oestrone Methyl Ether.*

By A. D. CROSS, H. CARPIO, and P. CRABBÉ.

Nuclear magnetic resonance spectral studies and chemical transformations have shown that the by-product of 9(11)-dehydrogenation of oestrone methyl ether (I) with chloranil in dioxan containing t-butyl alcohol is the dihydrophenanthrene (II; R = CO<sub>2</sub>Bu<sup>t</sup>). The effects of ring currents on the resonance frequencies of protons attached to the rings, or substituents, of phenanthrenes and 9,10-dihydrophenanthrenes are discussed.

RECENTLY there have been developed in our Laboratories two methods for the preparation of steroid-1,3,5(10),9(11)-tetraenes.<sup>2,3</sup> The second of these procedures involves prolonged treatment of a steroid-1,3,5(10)-triene with chloranil in boiling dioxan containing t-butyl alcohol. Thus, oestrone methyl ether (I) was readily converted into the 9(11)-unsaturated analogue [I; 9(11)-double bond].<sup>3</sup> Chromatography of the products furnished first a substance which showed strong ultraviolet absorption at 280 m $\mu$  and strong infrared absorption at 1735 cm.<sup>-1</sup>. Our initial conclusion that this substance was 3-methoxyoestra-1,3,5(10),8-tetraen-17-one [I; 8(9)-double bond] became suspect when analyses of a sublimed sample consistently indicated a C<sub>16</sub> or C<sub>23</sub> molecular formula. The situation was further complicated by the fact that the alcohol resulting from reduction of this by-product by lithium aluminium hydride, and the derived monoacetate, had analyses in agreement with C<sub>19</sub> and C<sub>21</sub> molecular formulæ, respectively.

Nuclear magnetic resonance (n.m.r.) spectroscopic examination\* of the chloranil dehydrogenation by-product, the derived alcohol, and the acetate of the latter (Figure and Table) established incontrovertibly the structures of these three substances as (II; R = CO<sub>2</sub>Bu<sup>t</sup>, CH<sub>2</sub>·OH, and CH<sub>2</sub>·OAc, respectively). A striking feature of the n.m.r. spectrum of the by-product (II; R = CO<sub>2</sub>Bu<sup>t</sup>) was the complete absence of the broad "hump" of resonances normally observed for steroids and associated with aliphatic protons.<sup>4</sup> Also of significance was an unsplit resonance at 8·530  $\tau$  (86·8 c./sec.) corresponding to nine magnetically equivalent protons. Assignment of the latter resonance to a t-butoxy-group received support from a mass-spectrometric determination of the molecular weight of the dehydrogenation by-product which gave a value, 352, higher by

\* N.m.r. frequencies are expressed as c./sec. downfield from the tetramethylsilane as internal reference for a 60 Mc./sec. oscillator. Coupling constants, *J*, are reported in c./sec. Accuracies are of the order of  $\pm 0\cdot025$   $\tau$  ( $\pm 1\cdot5$  c./sec.) for chemical shifts, and  $\pm 0\cdot5$  c./sec. for *J*.

<sup>1</sup> Part V, Knox, Velarde, Berger, Cuadriello, Landis, and Cross, *J. Amer. Chem. Soc.*, 1963, **85**, 1851. The present paper also constitutes Steroids. Part CCXXXVI. (Part CCXXXV, Villotti and Bowers, *Gazzetta*, in the press).

<sup>2</sup> Mills, Barrera, Olivares, and García, *J. Amer. Chem. Soc.*, 1960, **82**, 5882.

<sup>3</sup> Denot, Alvarez, Necoechea, and Bowers, unpublished work.

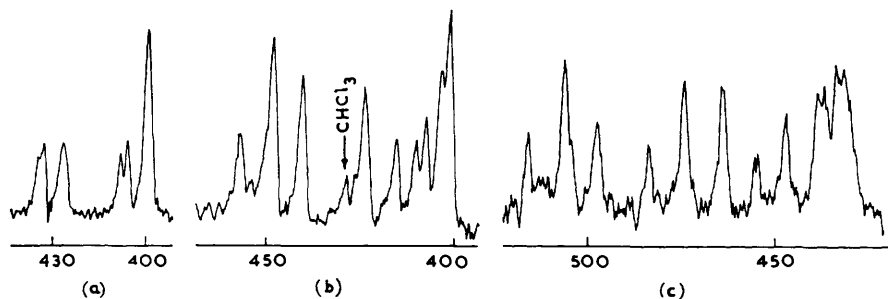
<sup>4</sup> Shoolery and Rogers, *J. Amer. Chem. Soc.*, 1958, **80**, 5121.

N.m.r. data \* for œstrone methyl ether and related biphenyls and phenanthrenes.

Compound	18-Me	3-OMe	Benzylic protons	C <sub>16</sub> protons	Other non aromatic protons
I	9.11 (53.7)	6.24 (225.5)	7.08 (166—184) C <sub>6</sub> and C <sub>9</sub> -protons	§	§
II; R = CO <sub>2</sub> Bu <sup>t</sup>	7.67 (139.6)	6.24 (225.5)	7.21 (167) C <sub>6</sub> and C <sub>7</sub> protons 7.03 (165—192), m. C <sub>15</sub> -protons	7.55 (137—157), m.	8.53 (86.8) t-butoxy-protons
II; R = CH <sub>2</sub> ·OH	7.69 (138.4)	6.26 (224.6)	7.24 (165.6) C <sub>6</sub> and C <sub>7</sub> -protons 7.28 (152—174), m. C <sub>15</sub> -protons	8.17 (91—117), m.	6.35 (212.9, 219.1, and an obscured peak), t. J <sub>16, 17</sub> = 6.2 C <sub>17</sub> -protons
II; R = CH <sub>2</sub> ·OAc	7.69 (138.7)	6.23 (226.0)	7.23 (167) C <sub>6</sub> - and C <sub>7</sub> -protons 7.25 (154—176), m. C <sub>15</sub> -protons	~8.17 (90—120), m. (and further observed resonance)	5.90 (240.0, 246.1, and 252.3), t. J <sub>16, 17</sub> = 6.1 C <sub>17</sub> -protons
III; † R = CO <sub>2</sub> Bu <sup>t</sup>	7.49 (150.8)	6.10 (234.3)	6.58 (193—218), m. C <sub>15</sub> -protons	7.48 (140—163), m.	8.53 (88.5) t-butoxy-protons
III; ‡ R = CH <sub>2</sub> ·OH	7.50 (149.9)	6.10 (233.8)	6.60 (180—204), m. C <sub>15</sub> -protons	8.12 (91—135), m.	6.25 (219.2, 225.2, and 231.2), t. J <sub>16, 17</sub> = 6.0 C <sub>17</sub> -protons
Compound	C <sub>1</sub> -proton ¶	C <sub>2</sub> -proton ¶	C <sub>4</sub> -proton	C <sub>11</sub> -proton	C <sub>12</sub> -proton
I	2.82 (426.7 and 434.5) J <sub>1, 2</sub> = 7.8, J <sub>1, 4</sub> = ca. 1	~3.30 (~398, and 405.1) J <sub>1, 2</sub> = ~7.5, J <sub>2, 4</sub> = 2.5	3.37 (398) broad "singlet"	§	§
II; R = CO <sub>2</sub> Bu <sup>t</sup>	~2.45 (obscured, ~449 and 456.4) J <sub>1, 4</sub> = <1, J <sub>1, 2</sub> = ~7.5	~3.25 (obscured doublet ~401; 407.5 and 409.5) J <sub>2, 4</sub> = 2, J <sub>1, 2</sub> = ~7.5	3.30 (401.0 and 403.0) d. J <sub>2, 4</sub> = 2.0	2.61 (439.6 and 447.6) J <sub>11, 12</sub> = 8.0	3.02 (415.0 and 423.2) J <sub>11, 12</sub> = 8.2
II; R = CH <sub>2</sub> ·OH	2.46 (449 and 456.4) J <sub>1, 2</sub> = 7.4, J <sub>1, 4</sub> = <1	~3.26 (obscured doublet ~400 and 402; 407.0 and 409.0) J <sub>2, 4</sub> = 2.0, J <sub>1, 2</sub> = ~7	3.32 (400.0 and 402.0), d. J <sub>2, 4</sub> = 2.0	2.62 (439 and 446.8) J <sub>11, 12</sub> = 7.8	3.02 (414.8 and 422.6) J <sub>11, 12</sub> = 7.8
II; R = CH <sub>2</sub> ·OAc	~2.44 (an obscured resonance ~450, and 457.3) J <sub>1, 2</sub> = ~7, J <sub>1, 4</sub> = <1	~3.24 (obscured doublet ~402; 407.9, and 409.9) J <sub>2, 4</sub> = 2.0, J <sub>1, 2</sub> = ~7	3.30 (401.1 and 403.1), d. J <sub>2, 4</sub> = 2.0	2.60 (440.1 and 448.0) J <sub>11, 12</sub> = 7.9	3.00 (416.0 and 423.8); J <sub>11, 12</sub> = 7.8 J <sub>12, 18</sub> = ~1
III; † R = CO <sub>2</sub> Bu <sup>t</sup>	~1.50 (an obscured resonance at ~506, and 513.5) J <sub>1, 2</sub> = ~7.5, J <sub>1, 4</sub> = <1	~2.76 (429.8 and an obscured resonance; 436.8 and 438.6) J <sub>1, 2</sub> = ~7, J <sub>2, 4</sub> = 1.8	2.80 (431.2 and 433.3), d. J <sub>2, 4</sub> = 2.1	1.65 (497.7 and 505.8) J <sub>11, 12</sub> = 8.1	~2.62 (447.1 and obscured resonance ~439) J <sub>11, 12</sub> = ~8
III; ‡ R = CH <sub>2</sub> ·OH	1.50 (507.0 and 514.3) J <sub>1, 2</sub> = 7.3, J <sub>1, 4</sub> = <1	~2.78 (429.0 and an obscured resonance ~431; 436.0 and 437.9) J <sub>1, 2</sub> = 7, J <sub>2, 4</sub> = 1.9	2.83 (429.6 and 431.5), d. J <sub>2, 4</sub> = 1.9	1.67 (495.8 and 504.0) J <sub>11, 12</sub> = 8.2	2.64 (437.5 and 445.6) J <sub>11, 12</sub> = 8.1

\* Data are presented as chemical shifts, measured in  $\tau$  units with the components of each resonance expressed as c./sec. in parentheses. d = doublet, t = triplet, m = multiplet. All other resonances are singlets, except where stated otherwise. ~ indicates that the measurement of an accurate value was not possible. † This spectrum also shows a quartet at 2.19  $\tau$  (454.3, 463.6, 474 and 483.5),  $J_{6,7} = 9.5$ , for the protons at C<sub>6</sub> and C<sub>7</sub>. ‡ This spectrum also shows a quartet at 2.23  $\tau$  (450.7, 460.1, 472.5, and 481.9),  $J_{6,7} = 9.4$ , for the protons at C<sub>6</sub> and C<sub>7</sub>. § Not resolved from surrounding resonances. ¶ Pair of doublets. || The C<sub>11</sub>- and C<sub>12</sub>-proton resonances constitute an AB quartet. The centre of gravity of each resonance has been calculated by the method of Bernstein, Pople, and Schneider, *Canad. J. Chem.*, 1957, **35**, 65.

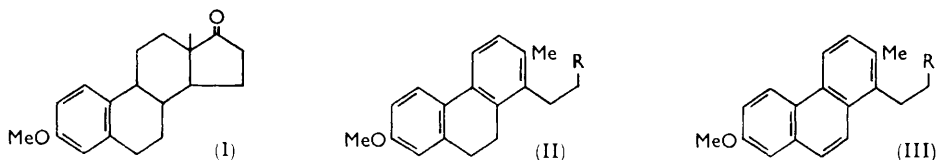
72 units than is required for 3-methoxyœstra-1,3,5(10),8-tetraen-17-one [I; 8(9)-double bond]. That ring A had undergone little or no structural changes was indicated by the similar frequencies of the methoxyl proton resonance of the t-butyl ester (II; R = CO<sub>2</sub>Bu<sup>t</sup>) and œstrone 3-methyl ether (Table). On the other hand, the 18-methyl-proton resonance was shifted by *ca.* 1.43  $\tau$  (85 c./sec.), and the ring A aromatic proton resonances



Aromatic proton resonances of (a) œstrone methyl ether (I), (b) the "biphenyl" (II; R = CO<sub>2</sub>Bu<sup>t</sup>), and (c) the phenanthrene (III; R = CO<sub>2</sub>Bu<sup>t</sup>).

were moved downfield, consistent with the introduction of further conjugated unsaturation into the steroid nucleus (see below). The appearance of two additional aromatic proton resonances as an AB quartet, when considered together with the strong shift of the 18-methyl resonance, led us to conclude that ring c had acquired aromatic character. Structure (II; R = CO<sub>2</sub>Bu<sup>t</sup>) was therefore deduced for the chloranil dehydrogenation by-product. All other resonances in the n.m.r. spectrum were compatible with this assignment.

Examination by the n.m.r. method of the alcohol (II; R = CH<sub>2</sub>·OH) obtained by reduction of the t-butyl ester (II; R = CO<sub>2</sub>Bu<sup>t</sup>), and of the corresponding acetate (II; R = CH<sub>2</sub>·OAc), confirmed the presence of the 1,2,7-trisubstituted 9,10-dihydrophenanthrene nucleus and of the propionic acid side-chain\* (Table). In the n.m.r. spectrum of the alcohol (II; R = CH<sub>2</sub>·OH) the C<sub>17</sub> 2-proton resonance appeared as a well-resolved



triplet,  $J_{16,17}$  6.2 c./sec., consistent with the presence of the structural unit CH<sub>2</sub>-OH with free rotation about the carbon-carbon bond. A triplet,  $J_{16,17}$  6.0 c./sec. was also observed for the acetate (II; R = CH<sub>2</sub>·OAc), for which it is shifted downfield by 0.45  $\tau$  (27 c./sec.) in accordance with expectation.<sup>4</sup> The clean resolution of these resonance triplets stands in contrast to the ill-resolved triplet commonly observed for the 17 $\alpha$ -proton of 17 $\beta$ -substituted steroids unsubstituted at positions 15 and 16 and retaining an intact ring D.<sup>4</sup>

Alkaline saponification of the t-butyl ester (II; R = CO<sub>2</sub>Bu<sup>t</sup>) afforded the acid (II; R = CO<sub>2</sub>H). In this, as in the other dihydrophenanthrenes (II), the absence of asymmetric centres was revealed in the near-zero optical rotations. [Neither this nor the absence of Cotton effect which seems to indicate a mixture of (*R*)- and (*S*)-isomers,<sup>5</sup> has been

\* In the remainder of the discussion the carbon skeleton of the dihydrophenanthrenes will be numbered as in steroids to emphasise the structural correlation with their precursors.

<sup>5</sup> Mislow, Glass, O'Brien, Rutkin, Steinberg, Weiss, and Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455, and other papers in this series.

investigated further.] Neither the ester (II; R = CO<sub>2</sub>Bu<sup>t</sup>) nor the alcohol (II; R = CH<sub>2</sub>·OH) was reduced by hydrogen and Adams platinum catalyst in the presence of perchloric acid. Oxidation of the ester by t-butyl chromate in carbon tetrachloride solution afforded the phenanthrene ester (III; R = CO<sub>2</sub>Bu<sup>t</sup>), in turn hydrolysed to the propionic acid (III; R = CO<sub>2</sub>H). Similarly the alcohol (II; R = CH<sub>2</sub>·OH) was oxidised by t-butyl chromate or dehydrogenated by dichlorodicyanoquinone, to the corresponding phenanthrene alcohol (III; R = CH<sub>2</sub>·OH). The latter showed the series of strong ultraviolet maxima characteristic of the phenanthrene ring system (see Experimental section).

Analyses of the aromatic proton resonance patterns have been made (Table; Figure) beginning with œstrone 3-methyl ether (I) for which the values  $J_{1,2} = 7.8$ ,  $J_{1,4} = ca. 1$ , and  $J_{2,4} = 2.5$  c./sec. were measured. The larger *meta*-coupling permitted identification of the C<sub>2</sub>- and C<sub>4</sub>-proton resonances at higher fields than the C<sub>1</sub>-proton resonance. In all spectra, irrespective of the degree of aromatisation of the tricyclic nucleus, the resonance corresponding to the C<sub>4</sub>-proton always obscured the higher-field doublet of the pair of doublets which constitute the C<sub>2</sub>-proton resonance. (The C<sub>4</sub>-proton resonance is split by coupling with the C<sub>2</sub>-proton and also by the smaller coupling with the C<sub>1</sub>-proton. Combined with the fact that this resonance lies over the higher-field doublet of the C<sub>2</sub>-proton resonance it is not surprising that the C<sub>4</sub>-proton resonance is observed, on a 500 c./sec. scan, as a broadened "singlet," of half-band width *ca.* 3.5 c./sec.) In the "biphenyl" derivatives (II) the two additional aromatic protons at positions 11 and 12 introduce a new AB quartet,  $J_{11,12} ca. 8$  c./sec., into the spectrum (Figure). Of this quartet the higher-field resonance at *ca.* 3.02  $\tau$  (415 and 423 c./sec.) is assigned to the C<sub>12</sub>-proton since in the spectrum of the acetate (II; R = CH<sub>2</sub>·OAc) this resonance showed a further small splitting ( $J ca. 1$  c./sec.), which is attributed to long-range coupling of the C<sub>12</sub>-proton with the methyl-protons at position 18. Moreover, the lower-field resonance at *ca.* 2.60  $\tau$  (440 and 448 c./sec.), which is assigned to the C<sub>11</sub>-proton resonance, shows a much greater frequency shift, 0.95  $\tau$  (57 c./sec.), on further dehydrogenation of the nucleus from a "biphenyl" (II) to a phenanthrene (III). This marked shift is paralleled by the C<sub>1</sub>-proton resonance which moves from *ca.* 2.45  $\tau$  (453 c./sec.) in the "biphenyls" (II) to *ca.* 1.50  $\tau$  (510 c./sec.) in the phenanthrenes (III) [shift = 0.95  $\tau$  (57 c./sec.)]. These proton resonance shifts may be rationalised in terms of the induced ring currents of the aromatic systems (I), (II), and (III). In the simplest case (I), with a single aromatic ring, the chemical shift between the C<sub>1</sub>- and C<sub>2</sub>-proton resonances has a value *ca.* 0.5  $\tau$  (30 c./sec.), an accurate evaluation being limited by C<sub>4</sub>-proton interference. Aromatisation of ring c, as in the "biphenyls" (II), leads to unequal extra deshielding of these protons, the downfield shift of the C<sub>2</sub>-proton resonance being only 0.05  $\tau$  (3 c./sec.) as against 0.37  $\tau$  (22 c./sec.) for the C<sub>1</sub>-proton, so that the latter resonance is now *ca.* 0.80  $\tau$  (48 c./sec.) to lower field from the C<sub>2</sub>-proton resonance. This extra deshielding of the C<sub>1</sub>-proton is due to its close proximity to the aromatic ring c and the magnitude of the shift indicates that the dihedral angle between rings a and c in the "biphenyls" (II) must be small. The same factors cause the pronounced chemical shift, *ca.* 0.4  $\tau$  (24 c./sec.) between the C<sub>11</sub>- and the C<sub>12</sub>-proton resonance. The C<sub>3</sub>-methoxyl group is primarily responsible for the larger chemical shift (*ca.* 0.5  $\tau$ ) between the C<sub>1</sub>- and C<sub>2</sub>-protons (see above). Goodwin, Shoolery, and Johnson<sup>6</sup> have described a similar case where the *o*-proton of a 2,2'-bridged biphenyl, the alkaloid dicentrine, resonates at much lower frequency than do other protons on the aromatic rings. In the phenanthrene analogues (III) rings a and c are completely coplanar and the induced ring currents are more powerful. Bernstein, Schneider, and Pople<sup>7</sup> analysed phenanthrenes and related systems and found the proton nearest to the greatest number of rings to have the lowest frequency. A comparison of the n.m.r. spectra of the esters (II; R = CO<sub>2</sub>Bu<sup>t</sup>) and (III; R = CO<sub>2</sub>Bu<sup>t</sup>) revealed the presence in the latter of an extra

<sup>6</sup> Goodwin, Shoolery, and Johnson, *Proc. Chem. Soc.*, 1958, 306.

<sup>7</sup> Bernstein, Schneider, and Pople, *Proc. Roy. Soc.*, 1956, A, 236, 515.

AB quartet for the new aromatic protons at C<sub>6</sub> and C<sub>7</sub> ( $J_{6,7}$  9.5 c./sec.) and further approximate downfield shifts of the other aromatic protons as follows: C<sub>4</sub>-proton, 0.5  $\tau$  (30 c./sec.); C<sub>2</sub>-proton, 0.5  $\tau$  (30 c./sec.); C<sub>1</sub>-proton, 0.95  $\tau$  (57 c./sec.); C<sub>11</sub>-proton, 0.97  $\tau$  (58 c./sec.); and C<sub>12</sub>-proton, 0.4  $\tau$  (24 c./sec.). Thus, the greatest shifts are those of the hindered proton frequencies, in agreement with prediction.<sup>7</sup> Increased aromaticity is also manifested in the downfield shifts of other proton resonances in the structural sequence (I)  $\longrightarrow$  (II; R = CO<sub>2</sub>Bu<sup>t</sup>)  $\longrightarrow$  (III; R = CO<sub>2</sub>Bu<sup>t</sup>) in which the number of aromatic rings rises from one to three. A study of the collected results shows a progressive shift of the 3-methoxyl proton resonance from 6.42  $\tau$  (225.5 c./sec.) to 6.24  $\tau$  (225.5 c./sec.) to 6.10  $\tau$  (234.3 c./sec.), and of the 18-methyl proton singlet from 9.11  $\tau$  (53.7 c./sec.) to 7.67  $\tau$  (139.6 c./sec.) to 7.49  $\tau$  (150.8 c./sec.). The benzylic proton resonances of the ester (II; R = CO<sub>2</sub>Bu<sup>t</sup>) appear as a broad 4-proton singlet at 7.21  $\tau$  (167 c./sec.) for the C<sub>6</sub>- and C<sub>7</sub>-methylenes, overlying a multiplet at 7.03  $\tau$  (165–192 c./sec.) for the protons at position 15. On aromatisation of ring B the singlet disappears and there is a downfield shift of the C<sub>15</sub>-proton multiplet to 6.58  $\tau$  (193–218 c./sec.). Other proton resonances are given in the Table.

No ring-D cleavage products could be isolated when oestrone methyl ether (I) was treated with chloranil in dioxan without t-butyl alcohol. However, the mechanism of formation of the dihydrophenanthrene ester (II; R = CO<sub>2</sub>Bu<sup>t</sup>) remains speculative since no evidence has yet been adduced favouring either heterolytic or homolytic 13,17-bond fission. The ability of t-butyl alcohol to form radicals and the potential stabilisation by electron delocalisation of charge, or a radical at position 13 following migration of a double bond from 9(11) to 11(12), may be pertinent factors.

#### EXPERIMENTAL

Except where stated otherwise, rotations are for chloroform solutions, ultraviolet spectral data are for ethanol solutions, and infrared data for potassium bromide discs.

M. p.s were determined on the Fisher-Johns block.

N.m.r. spectra were recorded on a Varian A-60 spectrometer operating at 60 Mc./sec., for 5–10% solutions in deuteriochloroform containing tetramethylsilane as an internal reference.

*t*-Butyl 3-Methoxy-13,17-secoœstra-1,3,5(10),8,11,13-hexaen-17-oate (II; R = CO<sub>2</sub>Bu<sup>t</sup>).—Oestrone methyl ether (1 g.) in solution in anhydrous dioxan (15 ml.) and t-butyl alcohol (45 g.) was treated with chloranil (4 g.) and kept under reflux for 40 hr. in a nitrogen atmosphere. After being cooled, the mixture was filtered and evaporated *in vacuo*, to afford a solid residue, a chloroform solution of which was washed several times with water, 10% aqueous sodium hydroxide, and again with water until neutral. Evaporation of the dried (Na<sub>2</sub>SO<sub>4</sub>) chloroform solution furnished a solid (890 mg.) which was chromatographed over neutral alumina (50 g.). Elution with hexane provided the *t*-butyl ester which on crystallisation from hexane and then sublimation had m. p. 101–102°,  $[\alpha]_D - 0.5^\circ$ ,  $\lambda_{\max}$  280 m $\mu$  (log  $\epsilon$  4.38),  $\nu_{\max}$  1735 cm.<sup>-1</sup> (Found: C, 78.4; H, 8.05; O, 13.4. C<sub>23</sub>H<sub>28</sub>O<sub>3</sub> requires C, 78.4; H, 8.0; O, 13.6%). Elution of the column with hexane-benzene (3:1) gave 3-methoxyœstra-1,3,5(10),9(11)-tetraen-17-one (508 mg.). A sample recrystallised from methylene chloride-hexane had m. p. 145–148°,  $[\alpha]_D + 298^\circ$ ,  $\lambda_{\max}$  264 m $\mu$  (log  $\epsilon$  4.26), identical with an authentic sample.<sup>3</sup>

3-Methoxy-13,17-secoœstra-1,3,5(10),8,11,13-hexaen-17-oic Acid (II; R = CO<sub>2</sub>H).—To the foregoing *t*-butyl ester (250 mg.) in methanol (20 ml.) and water (1 ml.) was added sodium hydroxide (250 mg.), and the mixture was kept under reflux during 24 hr., then poured into water. Extraction with ethyl acetate and separation into neutral and acid fractions furnished the acid, prisms (from acetone-hexane) (200 mg.), m. p. 174–175°,  $[\alpha]_D + 0^\circ$ ,  $\lambda_{\max}$  280 m $\mu$  (log  $\epsilon$  4.37),  $\nu_{\max}$  3300–2400 and 1695 (acid), 1610, 1585, 1555, and 1498 (conjugated aromatic ring), and 810 cm.<sup>-1</sup> (two adjacent aromatic protons) (Found: C, 77.05; H, 6.8; O, 16.35. C<sub>19</sub>H<sub>20</sub>O<sub>3</sub> requires C, 77.0; H, 6.8; O, 16.2%).

3-Methoxy-13,17-secoœstra-1,3,5(10),8,11,13-hexaen-17-ol (II; R = CH<sub>2</sub>·OH).—Reduction of the above *t*-butyl ester by lithium aluminium hydride in boiling tetrahydrofuran for 1 hr., followed by treatment of the mixture with ethyl acetate and then saturated aqueous sodium

sulphate, afforded, by the usual extraction procedure, the *alcohol* as prisms (from acetone-hexane), m. p. 93—94°,  $[\alpha]_D \pm 0^\circ$ ,  $\lambda_{\max}$  278—280  $m\mu$  ( $\log \epsilon$  4.36),  $\nu_{\max}$  3250, 1615, 1587, 1562, 1505, 872, 861, 816, and 806  $\text{cm}^{-1}$  (Found: C, 80.5; H, 7.55; O, 11.8.  $\text{C}_{19}\text{H}_{22}\text{O}_2$  requires C, 80.8; H, 7.85; O, 11.3%).

Acetylation furnished the *acetate* which, recrystallised from hexane, had m. p. 53—54°,  $[\alpha]_D \pm 0^\circ$ ,  $\lambda_{\max}$  280  $m\mu$  ( $\log \epsilon$  4.38),  $\nu_{\max}$  1739 and 1235 (OAc), 1605, 1560, 1500, 853, 848, and 813  $\text{cm}^{-1}$  (Found: C, 78.0; H, 7.55; O, 14.9.  $\text{C}_{21}\text{H}_{24}\text{O}_3$  requires C, 77.75; H, 7.5; O, 14.8%).

*t*-Butyl 3-Methoxy-13,17-*secoæstra*-1,3,5(10),6,8,11,13-*heptaen*-17-*oate* (III; R =  $\text{CO}_2\text{Bu}^t$ ).—The ester (II; R =  $\text{CO}_2\text{Bu}^t$ ) (500 mg.) in carbon tetrachloride (10 ml.), acetic anhydride (1.48 ml.), and acetic acid (0.55 ml.) was treated with *t*-butyl chromate reagent<sup>8</sup> and held under reflux for 18 hr., then cooled. 8.5% Aqueous oxalic acid (10 ml.) was added dropwise, followed by solid oxalic acid (700 mg.). Carbon tetrachloride extracts of the aqueous mixture were washed with water, 5% aqueous sodium hydrogen carbonate, and again water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. Several crystallisations of the residue from acetone-hexane gave the *phenanthrene ester*, m. p. 172—173°,  $[\alpha]_D -5^\circ$ ,  $\lambda_{\max}$  224—226, 236, 260, 280, 292, 302, 326, 340, and 358  $m\mu$  ( $\log \epsilon$  4.19, 4.21, 4.76, 4.18, 4.05, 3.86, 2.80, 3.02, and 3.04, respectively),  $\nu_{\max}$  1738 (ester), 1612, 1585, 1560, 1530, 1510, 1482, 880, 860, 816, 719, and 695  $\text{cm}^{-1}$  (Found: C, 79.0; H, 7.4; O, 13.8.  $\text{C}_{23}\text{H}_{26}\text{O}_3$  requires C, 78.8; H, 7.5; O, 13.7%).

3-Methoxy-13,17-*secoæstra*-1,3,5(10),6,8,11,13-*heptaen*-17-*ol* (III; R =  $\text{CH}_2\text{OH}$ ).—A solution of the alcohol (II; R =  $\text{CH}_2\text{OH}$ ) (250 mg.) and dichlorodicyanoquinone (750 mg.) in dioxan (7 ml.) was kept at room temperature for 20 hr., then diluted with methylene dichloride and filtered through Celite. Chromatography of the filtrate over alumina led to the *phenanthrene alcohol* which separated from acetone as prisms, m. p. 170—171°,  $[\alpha]_D +11^\circ$ ,  $\lambda_{\max}$  226, 236, 260, 279, 291, 302, 326, 340, 350, and 358  $m\mu$  ( $\log \epsilon$  4.30, 4.32, 4.84, 4.26, 4.13, 9.85, 2.85, 3.13, 2.81, and 3.16, respectively),  $\nu_{\max}$  3400, 1615, 1535, 1490, 861, 816, 738, and 720  $\text{cm}^{-1}$  (Found: C, 81.5; H, 7.0; O, 11.5.  $\text{C}_{19}\text{H}_{20}\text{O}_2$  requires C, 81.4; H, 7.2; O, 11.4%).

The same alcohol, prepared by *t*-butyl chromate oxidation of the precursor (II; R =  $\text{CH}_2\text{OH}$ ) as outlined above, had m. p. 165—167° undepressed on admixture with a sample prepared by the quinone procedure.

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RESEARCH LABORATORIES, SYNTEX, S.A., MEXICO, D.F.

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<sup>8</sup> Heusler and Wettstein, *Helv. Chim. Acta*, 1952, **35**, 284.