# Potentially Carcinogenic Cyclopenta[*a*]phenanthrenes. Part VII.[1] Ring-D Diols and Related Compounds

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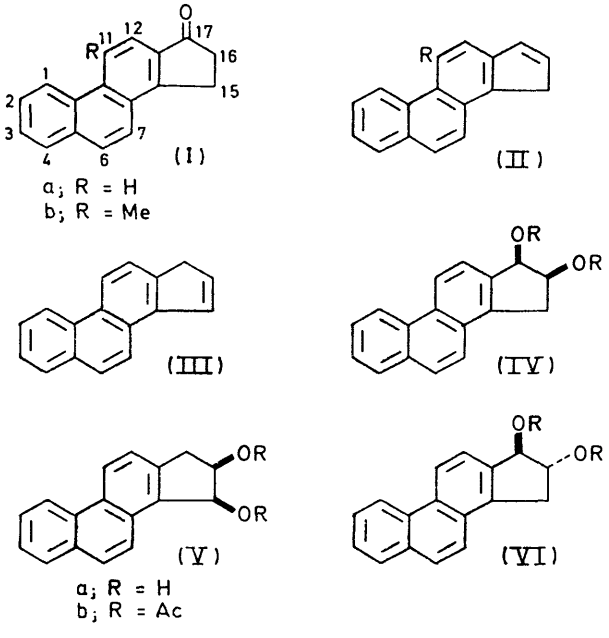
Elimination from 16,17-dihydro-17-tosyloxy-15*H*-cyclopenta[*a*]phenanthrene and from its 15-tosyloxy-isomer in dimethyl sulphoxide at 100° gave, respectively, 15*H*- and 17*H*-cyclopenta[*a*]phenanthrenes whereas, contrary to a previous report, elimination from the former in boiling collidine led to a 1 : 1 mixture of the two olefins. Dehydrogenation of 16,17-dihydro-15*H*-cyclopenta[*a*]phenanthrene with DDQ also led to a mixture of the 15*H*- and 17*H*-olefins. Elimination from 16,17-dihydro-11-methyl-17-tosyloxy-15*H*-cyclopenta[*a*]phenanthrene in boiling collidine yielded only the 11-methyl-15*H*-olefin. Oxidation of these olefins with osmium tetroxide gave *cis*-diols, whereas *trans*-diols were obtained by reduction of the corresponding 16-hydroxy-17-ketones with sodium borohydride. Unconjugated 16-ketones resulted from acid-catalysed dehydration of these diols.

METABOLIC studies on the potent carcinogen 15,16-dihydro-11-methylcyclopenta[*a*]phenanthren-17-one [2] (Ib) have implicated attack at the five-membered ring and prompted the work on synthetic ring-D oxygenated compounds described here.

In Part II [3] we claimed the synthesis of 15*H*-cyclopenta[*a*]phenanthrene (IIa) and the 17*H*-isomer (III), the former from the 17-tosylate in dimethyl sulphoxide at 100°, and the latter by elimination under more vigorous conditions in boiling collidine. The latter olefin was also prepared [3] by elimination from the 15-tosylate in boiling collidine. Both samples of olefins had the same m.p. and u.v. absorption characteristics as 17*H*-cyclopenta[*a*]phenanthrene reported by Süs [4] from




the decarboxylation of the 17-carboxylic acid. The former olefin (IIa) had u.v. absorption similar to that of the related 17-methyl-16(17)-ene.[3] In order to prepare the 16,17- and 15,16-diols these olefins were treated with osmium tetroxide. As expected, (IIa) gave the *cis*-16,17-diol (IVa) as sole product, but the supposed 17*H*-isomer yielded roughly equal amounts of two diols, one of which was identical with (IVa). The second compound was formulated as the *cis*-15,16-diol (Va), since its u.v. spectrum bore a strong resemblance to that of 15-hydroxy-16,17-dihydro-15*H*-cyclopenta[*a*]-phenanthrene.† The identity of (Va) was confirmed by the preparation of a specimen of 17*H*-cyclopenta-[*a*]phenanthrene by elimination from the tosylate in dimethyl sulphoxide at 100°. Addition of osmium tetroxide to this olefin gave a diol characterised as (Va) on the basis of mixed m.p. determinations of the derived diacetates. The u.v. spectra of the 15*H*- and 17*H*-isomers of cyclopenta[*a*]phenanthrene differ as previously described,[3] but the purer sample of the latter displays more intense absorption at 239 and 269 nm than reported.[3] It is therefore apparent that boiling either 15*H*- or 17*H*-cyclopenta[*a*]phenanthrene in collidine (b.p. 175°) leads to an equilibrium mixture containing roughly equal proportions of the two isomers and that the compound described previously as (III) was in reality a mixture of the two olefins. Dehydrogenation of 16,17-dihydro-15*H*-cyclopenta[*a*]phenanthrene with 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ) in boiling benzene also gave a mixture of the two olefins in good yield, but in this case the 15*H*-isomer predominated.

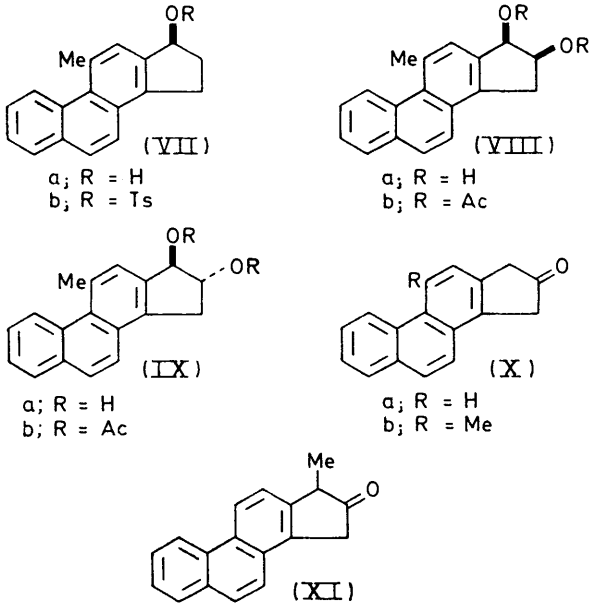
Reduction of 16-hydroxy-15,16-dihydrocyclopenta-[*a*]phenanthren-17-one [5] with sodium borohydride in methanol led to a high yield of a third diol, more polar and less soluble than (IVa). This was therefore assigned the *trans*-16,17-diol structure (VIa). A small quantity of the *cis*-diol (IVa) was identified chromatographically in the crude reduction products. Presumably co-ordination of the 16-hydroxy-group in the α-ketol with the borohydride directs attack by the latter on the carbonyl group from the side of the ring bearing the 16-oxygen atom, thus leading to a *trans* product.

16,17-Dihydro-11-methyl-15*H*-cyclopenta[*a*]phenanthren-17-ol (VIIa) was prepared by borohydride reduction of the ketone (Ib). Elimination from the

† Unpublished work.

[1] Part VI, M. M. Coombs and T. S. Bhatt, preceding paper.
[2] M. M. Coombs and C. J. Croft, *Progr. Exp. Tumor Res.*, 1969, **11**, 69.
[3] Part II, M. M. Coombs, *J. Chem. Soc.* (*C*), 1966, 963.
[4] O. Süs, *Annalen*, 1953, **579**, 133.
[5] Part III, M. M. Coombs, *J. Chem. Soc.* (*C*), 1969, 2484.

derived 17-tosylate (VIIb) in boiling collidine gave an olefin which displayed no u.v. absorption at 238 nm; the spectrum was similar to that of the known 11,17-dimethyl-16(17)-ene.[3] That this olefin was 11-methyl-




15*H*-cyclopenta[*a*]phenanthrene (IIb), unaccompanied by its 17*H*-isomer, was established by oxidation with osmium tetroxide to yield a single *cis*-diol (VIIIa). Thus the presence of the 11-methyl group appears to fix the position of the ring-D double bond in this olefin (IIb). The more polar and higher melting 11-methyl-*trans*-16,17-diol (IXa) was obtained as before by borohydride reduction of 15,16-dihydro-16-hydroxy-11-methylcyclopenta[*a*]phenanthren-17-one.[5] In this case also the *cis*-diol (VIIIa) was a minor reduction product.

The two pairs of *cis*- and *trans*-16,17-diols are readily distinguished by comparison of the n.m.r. spectra of their diacetates, as shown in the Table. In particular, separation of the chemical shifts between the two quartets due to the two non-equivalent C-15 protons is substantially smaller for the *cis*-diacetates than for the *trans*-isomers.

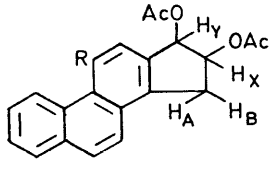
Acid catalysed dehydration of the mixture of 15,16- and 16,17-*cis*-diols (IVa) and (Va) furnished a single product, the 16-ketone (Xa), analogous to the unconjugated ketone formed on similar dehydration of indane-1,2-diol.[6] The structure of (Xa) follows from its u.v. absorption characteristics, which are similar to those of 16,17-dihydro-15*H*-cyclopenta[*a*]phenanthrene. In addition, the i.r. stretching frequency of the 16-carbonyl double bond occurs at 1750 $cm^{-1}$, similar to that of the 16-carbonyl group in the 17-methyl-16-ketone (XI) prepared by dehydration of the 17-methyl-16,17-diol.[7] Dehydration of the 11-methyl-16,17-diol (IXa) gave the 11-methyl-16-ketone (Xb), a positional isomer of the potent carcinogen (Ib).

## EXPERIMENTAL

Reagents and apparatus were generally as described in previous Parts of this series. T.l.c. was performed on plates coated with Kieselgel G (Merck) and dried overnight in air. Solutions in organic solvents were dried over anhydrous sodium sulphate.

*Reactions of* 15H- *and* 17H-*Cyclopenta*[a]*phenanthrenes with Osmium Tetroxide.—Comparative experiment.* Samples (10 mg) of 15*H*-cyclopenta[*a*]phenanthrene and the olefin designated as the '17*H*-isomer' in Part II were separately dissolved in portions (0·5 ml) of a solution in benzene of $OsO_4$,2py [containing osmium tetroxide (254 mg, 1 mmol) and pyridine (160 mg, 2 mmol) in 10·0 ml]. After 20 h the supernatant liquids were pipetted off and the brown precipitates were heated for 1·5 h on a steam-bath, each with pyridine (0·5 ml), water (0·2 ml), and sodium pyrosulphite (0·2 g). Addition of more water (15 ml) gave grey suspensions which were extracted with ether, yielding, in both cases, white solids. That from the 15*H*-olefin gave, on t.l.c. (ethanol–toluene, 1 : 5), one spot, $R_F$ 0·43; the solid from the 17*H*-olefin exhibited two spots, $R_F$ 0·43 and 0·46, of similar intensity. These solids were separately acetylated with acetic anhydride (1·0 ml) in pyridine

N.m.r. chemical shifts (τ) and coupling constants (Hz) of protons attached to the D-ring in 16,17-diacetates




| | | R | C-15 $H_A$ | C-15 $H_B$ | C-15 $H_A - H_B$ | C-16 $H_X$ | C-17 $H_Y$ | OAc |
|---|---|---|---|---|---|---|---|---|
| *cis*-Diacetate | (IVb) | H | 6·58(q) $J_{AB}$ 16 $J_{AX}$ 5 | 6·30(q) $J_{AB}$ 16 $J_{BX}$ 7 | 0·28 | 4·28(q) | 3·58(d) $J_{XY}$ 6 | 7·91(s), 7·89(s) |
| *cis*-Diacetate | (VIIIb) | Me | 6·65(q) $J_{AB}$ 16 $J_{AX}$ 4 | 6·36(q) $J_{AB}$ 16 $J_{BX}$ 6 | 0·29 | 4·31(q) | 3·61(d) $J_{XY}$ 6 | 7·92(s), 7·88(s) |
| *trans*-Diacetate | (VIb) | H | 6·78(q) $J_{AB}$ 16 $J_{AX}$ 4 | 6·07(q) $J_{AB}$ 16 $J_{BX}$ 8 | 0·71 | 4·39(quint) | 3·54(d) $J_{XY}$ 4 | 7·90(s), 7·86(s) |
| *trans*-Diacetate | (IXb) | Me | 6·84(q) $J_{AB}$ 17 $J_{AX}$ 4 | 6·10(q) $J_{AB}$ 17 $J_{BX}$ 8 | 0·74 | 4·42(quint) | 3·58(d) $J_{XY}$ 4 | 7·92(s), 7·87(s) |

[6] C. W. J. Brooks and L. Young, *Biochem. J.*, 1956, **63**, 264.
[7] H. Dannenberg, D. Dannenberg-von Dresler, and H.-G. Neumann, *Annalen*, 1960, **636**, 74.

(1·0 ml) for 18 h at room temperature. After addition of water (10 ml) and refrigeration for 3 h the precipitates were collected, washed with water, and dried. Each weighed 8 mg. That from the 15*H*-olefin had m.p. 167—172° and its i.r. spectrum was identical with that of the *cis*-16,17-diacetate, m.p. 173—175° (see later). The solid from the '17*H*-olefin' melted between 140 and 155°.

*Preparative experiment.* Osmium tetroxide (540 mg) was added to the '17*H*-olefin' (454 mg) (Part II) dissolved in pyridine (5·0 ml); the solution became dark and a solid separated. After 2 h sodium pyrosulphite (1·0 g) in water (5·0 ml) was added, and the mixture was kept for a further 30 min with frequent shaking. Addition of water (200 ml) gave an orange solution containing cream-coloured solid which was filtered off, washed with water, and dried (465 mg). This mixture of diols (two adjacent spots on t.l.c.) was acetylated as already described yielding a crystalline solid (567 mg), m.p. 143—150°. Chromatography on a column of silica gel (60 × 2 cm diam.) with hexane containing increasing proportions of dichloromethane led to the separation of two compounds. The faster-running (125 mg), m.p. 188—189°, was recrystallised from ethanol to furnish cis-15,16-*diacetoxy*-16,17-*dihydro*-15H-*cyclopenta*[a]*phenanthrene* (Vb), m.p. 189—191° (Found: C, 75·3; H, 5·5. $C_{21}H_{18}O_4$ requires C, 75·45; H, 5·45%), $\lambda_{max.}$ (EtOH) 223 (log ε 4·29), 255 (4·76), 279 (4·13), 287·5 (4·06), 299·5 (4·11), 319 (2·58), 325·5 (2·49), 334 (2·59), 340 (2·35), and 350 nm (2·23), $\nu_{max.}$ (Nujol) 1730 (Ac), 820, and 755 $cm^{-1}$. In the same way the slower-running material (144 mg) gave cis-16,17-*diacetoxy*-16,17-*dihydro*-15H-*cyclopenta*[a]*phenanthrene* (IVb), m.p. 173—175° (Found: C, 75·4; H, 5·3%), $\lambda_{max.}$ (EtOH) 249·5 (log ε 4·74), 256·5 (4·87), 278·5 (4·20), 286 (4·09), 298 (4·18), 319·5 (2·63), 327·5 (2·48), 334·5 (2·82), 343 (2·43), and 350 nm (2·82), $\nu_{max.}$ (Nujol) 1738 (Ac) 817, and 754 $cm^{-1}$.

16,17-*Dihydro*-15H-*cyclopenta*[a]*phenanthrene*-cis-16,17-*diol* (IVa).—The *cis*-diacetate (IVb) (105 mg), m.p. 160—165°, contaminated with a small quantity of the *cis*-15,16-isomer, was dissolved in ethanol (5 ml) and water (0·5 ml) and kept at ambient temperature for 20 h with potassium hydroxide (100 mg). Addition of more water (10 ml) gave a crystalline precipitate of the cis-16,17-*diol* (IVa), m.p. 226—228° (Found: C, 81·3; H, 5·25. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·65%), $R_F$ 0·50 (ethanol–toluene, 1 : 4), $\lambda_{max.}$ (EtOH) 250·5 (log ε 4·71), 257 (4·83), 279 (4·16), 287 (4·06), 299 (4·16), 320 (2·71), 327·5 (2·56), 334·5 (2·87), 343 (2·49), and 350 nm (2·86), $\nu_{max.}$ (Nujol) 3285 (OH), 823, 817, 750, and 742 $cm^{-1}$.

16,17-*Dihydro*-15H-*cyclopenta*[a]*phenanthrene*-trans-16,17-*diol* (VIa).—15,16-Dihydro-16-hydroxycyclopenta[*a*]phenanthren-17-one (1·20 g) was stirred in methanol (40 ml) during the addition of sodium borohydride (1 g). After 1 h, more sodium borohydride (1 g) was added and stirring was continued for a further 2 h. Dilution with water (60 ml) gave a precipitate which was collected, washed with water, and dried. The cream solid (0·951 g) was shown by t.l.c. (ethanol–toluene, 1 : 4) to consist mainly of a substance with $R_F$ 0·44, together with a small amount of the *cis*-16,17-diol, $R_F$ 0·50. Crystallisation of this solid from n-butanol gave the trans-16,17-*diol* (VIa), m.p. 277—278° (Found: C, 81·2; H, 5·55. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·65), $\lambda_{max.}$ (EtOH) 250·5 (log ε 4·71), 257 (4·82), 279 (4·16), 287 (4·05), 299 (4·17), 320 (2·65), 327·5 (2·49), 335 (2·84), 343 (2·44), and 350 nm (2·84), $\nu_{max.}$ (Nujol) 3260 (OH), 824, and 744 $cm^{-1}$. The trans-16,17-*diacetate* (VIb), prepared by treatment with acetic anhydride–pyridine at room temperature for 20 h, crystallised from ethanol in prisms, m.p. 159—160° (Found: C, 75·3; H, 5·1. $C_{21}H_{18}O_4$ requires C, 75·45; H, 5·45%), $\lambda_{max.}$ (EtOH) 249·5 (log ε 4·74), 256·5 (4·88), 278·5 (4·17), 286·5 (4·06), 298·5 (4·18), 319 (2·64), 327 (2·51), 334 (2·83), 342 (2·45), and 350 nm (2·80), $\nu_{max.}$ (Nujol) 1730 (Ac), 825, and 757 $cm^{-1}$.

17H-*Cyclopenta*[a]*phenanthrene* (III).—16,17-Dihydro-15*H*-cyclopenta[*a*]phenanthren-15-ol [8] (175 mg), dissolved in dry pyridine (3 ml), was kept with toluene-*p*-sulphonyl chloride (142 mg) for 3 h. After dilution with water (50 ml), the mixture was extracted with dichloromethane and the extract was washed successively with 2N-sulphuric acid, aqueous sodium hydrogen carbonate, and water, and dried. Removal of the solvent gave the crude tosylate as a gum (137 mg) which was dissolved in dimethyl sulphoxide (0·2 ml) and heated on a steam-bath for 1 h. The solvent was removed *in vacuo*, and the residual gum was triturated with hexane–dichloromethane (10 : 1). The extract (46 mg) was purified by preparative t.l.c. (hexane–benzene, 4 : 1) on three 20 × 20 cm plates to furnish 17*H*-cyclopenta[*a*]phenanthrene (III) (12 mg) as a white solid, $\lambda_{max.}$ (EtOH) 238 (log ε 4·11), 268·5 (4·46), 273 (4·42), 291·5 (3·93), 302 (3·91), 314·5 (2·82), 343 (2·45), and 360 nm (2·44). Repetition of the dimethyl sulphoxide treatment with the hexane–dichloromethane-insoluble material gave a further quantity of (III) (5 mg).

This olefin (12 mg) was treated with osmium tetroxide as already described. The product was a cream solid (11·5 mg) which had the same $R_F$ as (Va). Acetylation gave crystals, m.p. 168—171°, with the same $R_F$ as (Vb). Mixed m.p. with a sample of (Vb) (m.p. 189—191°) was 182—185°, and with a sample of (IV) (m.p. 173—175°) was 149—160°.

*Dehydrogenation of* 16,17-*Dihydro*-15H-*cyclopenta*[a]-*phenanthrene with* 2,3-*Dichloro*-5,6-*dicyano*-1,4-*benzoquinone*.—The dihydro-compound (80 mg) was heated under reflux with a solution of DDQ (100 mg) in dry benzene (10 ml) for 20 h. The precipitate was filtered off and the filtrate was evaporated to dryness. The resulting solid was chromatographed on a column of alumina (Woëlm, grade IV; 5 g.) with hexane–benzene (4 : 1) to yield 15*H*-(and 17*H*-)cyclopenta[*a*]phenanthrene (53·3 mg), $\lambda_{max.}$ (EtOH) 239 (log ε 4·026), 269 (4·798), and 273·5 nm (4·803).

A sample (10 mg) of this olefin was treated with osmium tetroxide as described in the comparative experiment. The isolated diol (8 mg) gave a major spot, $R_F$ 0·43, and a minor spot at $R_F$ 0·46, on t.l.c. as already described. After acetylation the product (6 mg) melted at 155—165° (*cf.* with mixed m.p.s in the previous section).

16,17-*Dihydro*-11-*methyl*-15H-*cyclopenta*[a]*phenanthren*-17-*ol* (VIIa).—15,16-Dihydro-11-methylcyclopenta[*a*]phenanthren-17-one (0·50 g), sodium borohydride (0·50 g), tetrahydrofuran (30 ml), and water (2 ml) were boiled together under reflux for 18 h. Dilution with water gave a precipitate which was collected and dried (380 mg). Crystallisation from dichloromethane–hexane (1 : 1) afforded the 17-*ol* (VIIa) (220 mg), m.p. 140—141° (Found: C, 86·9; H, 6·8. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%), $\lambda_{max.}$ (EtOH) 227 (log ε 4·22), 255 (4·78), 281 (4·02), 293 (4·02), 304·5 (4·10), 323 (2·79), 338·5 (2·96), and 354 nm (2·98), $\nu_{max.}$ (Nujol) 3245 (OH), 825, 817, and 750 $cm^{-1}$.

[8] G. M. Badger, W. Carruthers, and J. W. Cook, *J. Chem. Soc.*, 1952, 4996.

11-*Methyl*-15H-*cyclopenta*[a]*phenanthrene* (IIb).—The 17-ol (VIIa) (424 mg), toluene-*p*-sulphonyl chloride (330 mg), and dry pyridine were kept together at room temperature for 2 h. After dilution with chloroform (30 ml) the solution was washed as already described to yield the tosylate (VIIb) as a resinous brown solid (335 mg), $\nu_{max.}$ (Nujol) 1030 and 1010 $cm^{-1}$, characteristic of tosylates. This derivative, dissolved in collidine (5·0 ml), was boiled under reflux for 30 min, and worked up as already described to give an oil (360 mg) showing no u.v. absorption at 238 nm. After filtration through a short column of alumina (Woëlm, grade II) in benzene–hexane (1 : 1) the product (275 mg) was an almost colourless oil which readily crystallised. A sample was sublimed at 100° and $10^{-3}$ mmHg, giving the *olefin* (IIb), m.p. 87—89° (Found: C, 93·6; H, 6·3. $C_{18}H_{14}$ requires C, 93·85; H, 6·15%), $\lambda_{max.}$ (EtOH) 221·5 (log ε 4·47), 267 (4·65), 274 (4·65), 294 (4·08), 306 (4·08), 317 (2·83), 348 (2·85), and 364 nm (2·74), $\nu_{max.}$ (Nujol) 815, 751, and 701 $cm^{-1}$.

16,17-*Dihydro*-11-*methyl*-15H-*cyclopenta*[a]*phenanthrene*-cis-16,17-*diol* (VIIIa).—A solution of the 15*H*-olefin (IIb) (115 mg, 0·5 mmol) in benzene (11·5 ml) was treated with osmium tetroxide (0·55 mmol) by the usual method; no solid separated from the brown solution. After 2 h, when t.l.c. demonstrated absence of olefin, the solvent was removed under diminished pressure and the residue was treated with sodium pyrosulphite as already described to yield a crystalline solid (135 mg) which ran as one spot, $R_F$ 0·59 (toluene–ethanol, 4 : 1) [the 11-methyl-*trans*-16,17-diol (IXa) had $R_F$ 0·55 when run alongside]. Repeated crystallisation from ethanol gave the diol (VIIIa), m.p. 181—182°, $\lambda_{max.}$ (EtOH) 227 (log ε 4·19), 255 (4·83), 281 (4·07), 292·5 (4·03), 304 (4·11), 323·5 (2·80), 338·5 (2·96), and 354 nm (2·94), $\nu_{max.}$ (Nujol) 3310 (OH), 1098, 820, and 743 $cm^{-1}$. Acetylation with pyridine–acetic anhydride at room temperature for 20 h gave the cis-*diacetate* (VIIIb), m.p. 192·5—193°, $\lambda_{max.}$ (EtOH) 226 (log ε 4·15), 254·5 (4·88), 281 (4·11), 292 (4·06), 303·5 (4·14), 323·5 (2·81), 338·5 (2·97), and 354 nm (2·98), $\nu_{max.}$ (Nujol) 1740, 1255, 1237, and 818 $cm^{-1}$, *m/e* 348·1366 ($M^+$) ($C_{22}H_{20}O_4$ requires 348·1362).

16,17-*Dihydro*-11-*methyl*-15H-*cyclopenta*[a]*phenanthrene*-trans-16,17-*diol* (IXa).—15,16-Dihydro-16-hydroxy-11-methylcyclopenta[*a*]phenanthren-17-one (1·00 g) was reduced with sodium borohydride as already described. The precipitate (0·59 g) formed on addition of water (60 ml) to the mixture consisted mostly of a substance, $R_F$ 0·46 (ethanol–toluene, 1 : 4). Crystallisation from ethanol yielded the 11-*methyl*-trans-16,17-*diol* (IXa), m.p. 224—226° (Found: C, 81·5; H, 6·05. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%), $\lambda_{max.}$ (EtOH) 227 (log ε 4·22), 256 (4·85), 281 (4·07), 292·5 (4·04), 305 (4·13), 323 (2·82), 338·5 (2·97), and 354 nm (2·98), $\nu_{max.}$ (Nujol) 3275 (OH), 1068, 825, and 745 $cm^{-1}$. Acetylation gave the diacetate (IXb), m.p. 156—157°, $\lambda_{max.}$ (EtOH) 224 (log ε 4·14), 254 (4·88), 280·5 (4·09) 292 (4·05), 304 (4·15), 323 (2·80), 338 (2·97), and 354 nm (2·97), $\nu_{max.}$ (Nujol) 1730, 1258, and 1240 $cm^{-1}$ (acetate). The material in the original mother liquor was shown by t.l.c. to consist of similar amounts of (IXa) and the *cis*-diol (VIIIa).

15,17-*Dihydro*-17-*methylcyclopenta*[a]*phenanthren*-16-*one* (XI).— 16,17-Dihydro-17-methyl-15*H*-cyclopenta[*a*]phenanthrene-16,17-diol [7] (235 mg) was heated on a steam-bath with 5N-sulphuric acid (10 ml) for 3 h. The solid was collected, washed with water, dried, and crystallised from benzene–hexane to furnish the 17-*methyl*-16-*one* (XI) as rosettes (80 mg), m.p. 184—185° (Found: C, 87·6; H, 6·1. $C_{18}H_{14}O$ requires C, 87·75; H, 5·75%). $\lambda_{max.}$ (EtOH) 259 (log ε 4·80), 278 (4·23), 288 (4·10), 300 (4·14), 319 (3·06), 334 (3·03), and 350 nm (2·96), $\nu_{max.}$ (Nujol) 1740 (CO), 818, and 748 $cm^{-1}$.

15,17-*Dihydrocyclopenta*[a]*phenanthren*-16-*one* (Xa).—A mixture (107 mg) of the 15,16-diacetoxy- and 16,17-diacetoxy-compounds from the osmium tetroxide oxidation was dissolved in methanol (10 ml) and water (2 ml) and heated on a steam-bath with potassium hydroxide (200 mg). After 75 min, 5N-sulphuric acid (50 ml) was added and heating was continued for 6 h. The cooled mixture was extracted with chloroform and the solid left on removal of the solvent was recrystallised twice from benzene with the addition of hexane to yield the *ketone* (Xa) as pale yellow rosettes of needles (10 mg), m.p. 172—174° (Found: C, 87·65; H, 5·1. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%), $\lambda_{max.}$ (EtOH) 258 (log ε 4·77), 269 (4·21), 278 (4·11), 300 (4·21), 319 (3·14), 335 (3·10), and 350 nm (3·03), $\nu_{max.}$ (Nujol) 1750 (CO), 833, 802, 768, and 748 $cm^{-1}$.

15,17-*Dihydro*-11-*methylcyclopenta*[a]*phenanthren*-16-*one* (Xb).—The 11-methyl-16,17-*trans*-diol (IXa) (203 mg) was boiled under reflux with tetrahydrofuran (10 ml) and 5N-sulphuric acid (10 ml) for 17 h. The cooled solution was extracted with benzene; the extract was washed with sodium hydrogen carbonate and dried. Evaporation gave a yellow gum (201 mg) which was purified by elution from a column of silica gel with dichloromethane. The *ketone* (Xb) (57 mg) formed pale yellow needles, m.p. 152·5—153°, $\lambda_{max.}$ (EtOH) 256·5 (log ε 4·77), 282 (4·06), 295 (4·08), 307 (4·16), 324 (2·99), 339 (3·06), and 355 nm (3·04), $\nu_{max.}$ (Nujol) 1740 (CO), 828, 795, and 743 $cm^{-1}$, *m/e* 264·1041 ($M^+$) ($C_{18}H_{14}O$ requires 246·1045).

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