Potentially Carcinogenic Cyclopenta[*a*]phenanthrenes (1,2-Cyclopentenophenanthrenes). Part I. A New Synthesis of 15,16-Dihydro-17-oxocyclopenta[*a*]phenanthrene and the Phenanthrene Analogue of 18-Norœstrone Methyl Ether

By M. M. Coombs

15,16-Dihydro-17-oxocyclopenta[*a*]phenanthrene and its 3-methoxy, 11- and 12-methyl, and 11,12-dimethyl derivatives have been synthesised by aromatisation of the 3-unsubstituted and 3-methoxy-11,17-diketones in which rings C and D are both saturated; the mechanism of the aromatisation is discussed.

RENEWED interest in 1,2-cyclopentenophenanthrene (16,17-dihydro-15*H*-cyclopenta[*a*]phenanthrene) (IX) has arisen in connection with the carcinogenic properties of certain members of this series structurally related to the natural steroids,[1,2] and it became of interest to devise syntheses of derivatives oxygenated at positions 3 and 17 (steroid numbering). Although several syntheses of the 17-oxo-derivative (VIa) have been described, they are not readily adapted to the preparation of nuclear-substituted derivatives. It has now been found that the diketones (Ia) and (Ib),* obtained by

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* The *trans* configuration of the C/D ring junction is assumed throughout (see Chinn *et al.*[3c]).

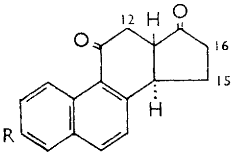
[1] H. Dannenberg, D. von Dresler, and H.-G. Neumann, *Annalen*, 1960, **636**, 74.

[2] H. Dannenberg, *Z. Krebsforsch.*, 1960, **63**, 523.

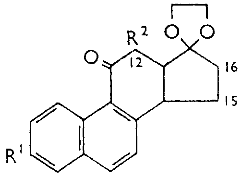
[3] (*a*) A. Koebner and R. Robinson, *J. Chem. Soc.*, 1938, 1994; (*b*) A. J. Birch, R. Jaeger, and R. Robinson, *ibid.*, 1945, 582; see also (*c*) L. J. Chinn, E. A. Brown, R. A. Mikulec, and R. B. Garland, *J. Org. Chem.*, 1962, **47**, 1733.

Robinson[3a,b] from furfuraldehyde and 2-acetyl- and 2-acetyl-7-methoxy-naphthalene, respectively, can be employed with advantage for the preparation of the required 17-oxo-derivative. A preliminary report of this work has appeared.[4]

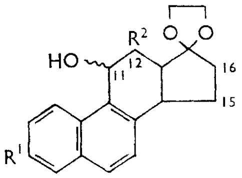
Selective ketalisation of the 17-carbonyl group in the diketone (Ia) was achieved by acid-catalysed exchange with ethylmethyldioxolan to give the oxo-ketal (IIa) in good yield. Under comparable conditions the 3-methoxy-diketone (Ib) was converted into a mixture of the 17-monoketal (IIb) and the 11,17-diketal (IVb); the corresponding diketal (IVa) was also obtained from (Ia) by prolonged exchange. These diketals were readily partially hydrolysed to the 17-monoketals with chloroform containing a trace of hydrochloric acid. The monoketals (IIa) and (IIb) exhibit typical aryl ketone infrared absorption at 6·0 μ and have ultraviolet spectra closely similar to those of the parent diketones. The diketals (IVa) and (IVb), on the other hand, lack infrared carbonyl absorption, while (IVa) has $\lambda_{max.}$ 229 and 280 mμ, characteristic of the unconjugated naphthalene chromophore in cyclopenta[*a*]phenanthrenes having rings C and D saturated. Reduction of the oxo-ketals (IIa) and (IIb) with sodium borohydride furnished the corresponding 11-hydroxy-17-ketals (IIIa) and (IIIb) as epimeric mixtures which were not further separated.



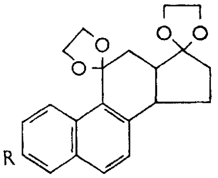
(Ia: R = H)
(Ib: R = OMe)



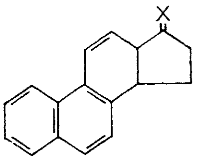
(IIa: R¹ = R² = H)
(IIb: R¹ = OMe, R² = H)
(IIc: R¹ = H, R² = Me)
(IId: R¹ = H, R² = CHO)
(IIe: R¹ = H, R² = CH_2·OH)



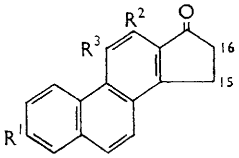
(IIIa: R¹ = R² = H)
(IIIb: R¹ = OMe, R² = H)
(IIIc: R¹ = H, R² = Me)
(IIId: R¹ = H, R² = CH_2·OH)



(IVa: R = H)
(IVb R = OMe)



(Va: X = O)
(Vb: X = $<^{H}_{OH}$)
(Vc: X = $<^{O}_{O}]$)
(Vd: X = H_2)



(VI)	R¹	R²	R³
a:	H	H	H
b:	OMe	H	H
c:	H	Me	H
d:	H	H	Me
e:	H	Me	Me
f:	H	H	OMe

When (IIIa) was boiled with acetic acid containing hydrochloric acid, instead of the expected product of dehydration and deketalisation, namely (Va), a mixture of (VIa) and its tetrahydro-derivative (VII) was obtained. Since this result pointed to the mutual oxidation–reduction of a common intermediate, the dehydration was repeated in the presence of a large excess of nitrobenzene; as expected, the fully oxidised product (VIa) was now obtained as the sole isolated product, in 86% yield. Under these conditions, with nitrobenzene and acid, the 11-hydroxy-3-methoxy-compound (IIIb) gave the ketone (VIb), the phenanthrene analogue of 18-nor-œstrone methyl ether, in 84% yield.

The diketone (Ia) was reduced with borohydride to the corresponding diol which was then heated with nitrobenzene and acid, as above. The product, however, was a complex mixture, chromatography of which yielded the unsaturated alcohol (Vb) as the main component (approximately 30% yield). A small amount of (IX) contaminated with the corresponding 15,16-dehydro-compound was also isolated, but only a trace of the expected 15,16-dihydro-17-hydroxycyclopenta[*a*]-phenanthrene was detected. Compound (Vb) had $\lambda_{max.}$ 239 and 315 mμ, characteristic of structure (IX) having additional hydrogen atoms at the C/D ring fusion positions (13,14); on catalytic reduction, followed by reoxidation of the saturated alcohol with the Jones reagent, the ketone (VII) was isolated, identical with that obtained above. Oxidation of the alcohol (Vb) with the Jones reagent gave the ketone (Va) in low yield, while oxidation with an excess of chromium trioxide in pyridine did not afford (Va), but (VIa) was readily isolated (68%). The unsaturated ketone (Va) was better prepared from the hydroxy-ketal (IIIa) through its tosylate which, on elimination, gave the ketal (Vc). Mild acid hydrolysis of the latter then led to (Va). This compound was very sensitive to acids and disproportionated completely to (VIa) and other products when the mild acid hydrolysis was prolonged. When the unsaturated ketal (Vc) was heated with nitrobenzene and acid, as described above, the sole product was (VIa) (91% yield); in the absence of nitrobenzene the yield was 43%. The compound (VII) was isolated (36%), together with its 13,14-dehydro-derivative[5,6] (22%), presumably formed by acid-catalysed isomerisation of the 13,14-dihydro-17-ketone to the fully conjugated 11,12-dihydro structure.

It therefore appears that a 17-carbonyl group is necessary for the easy dehydrogenation of the 13,14-dihydro-compounds. In order to investigate this further, compound (VIIIa)[7] was prepared and reduced to the

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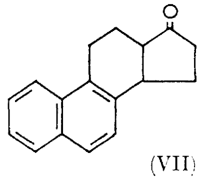
[4] M. M. Coombs, *Chem. and Ind.*, 1965, 270.

[5] W. S. Johnson and J. W. Peterson, *J. Amer. Chem. Soc.*, 1945, **67**, 1366.

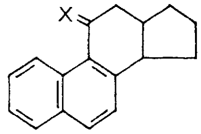
[6] A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson, and C. H. Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1985.

[7] A. Butenandt, H. Dannenberg, and D. von Dresler, *Z. Naturforsch.*, 1946, **1**, 151.

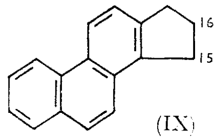
corresponding alcohol. The latter was then heated with acid, both with and without added nitrobenzene. The products from both reactions were similar complex mixtures consisting of about ten separate compounds as judged by thin-layer chromatography. The three least polar compounds were isolated and identified; from both experiments these were (VIIIc), (Vd), and (IX), in yields of 14, 3, and 20% (from reaction with $PhNO_2$), and 14, 10, and 20% (without $PhNO_2$). Thus, although limited aromatisation occurs, the extent to which it does so is not influenced by the addition of nitrobenzene, as is the case with the ketone (Va). With this compound it is suggested that dehydrogenation is initiated by abstraction of a hydride ion from C-14 in the enol (XIII), followed by bond rearrangement and the eventual loss of the second hydrogen atom as a proton. Further evidence for this mechanism is presented below.



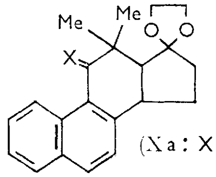
(VII)



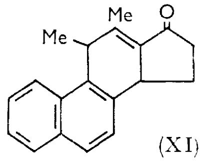
(VIIIa: X = O)
(VIIIb: X = $<^{H}_{OH}$)
(VIIIc: X = H_2)



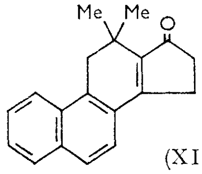
(IX)



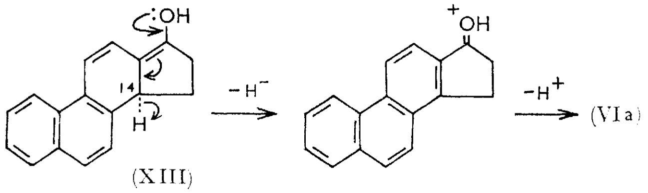
(Xa: X = O)
(Xb: X = $<^{H}_{OH}$)



(XI)



(XII)



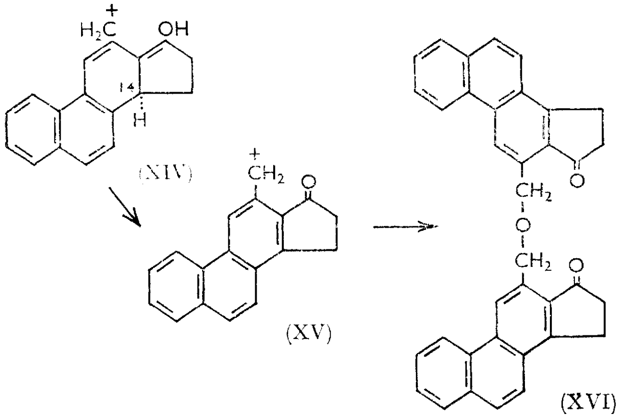
(XIII)

Methylation of the oxo-ketal (IIa) with methyl iodide and potassium t-butoxide gave mixtures of the 12-methyl (IIc) and 12,12-dimethyl (Xa) derivative depending on the ratios of reagents employed; methylation with 3 equivalents was most satisfactory, producing (IIc) in 62% yield. The ultraviolet spectra of (IIc) and (Xa) closely resembled that of the unsubstituted compound (IIa). The structure of (Xa) was further substantiated by the presence of its nuclear magnetic resonance (n.m.r.) spectrum of two unsplit methyl signals at τ 8·64 and 8·82. Both 12-methyl derivatives exhibited a marked tendency, probably associated with their cage-like structures, to occlude solvents, and reproducible analytical figures were obtained only after sublimation. These ketones also resisted reduction by borohydride, but were smoothly reduced to the corresponding alcohols (IIIc) and (Xb) with lithium aluminium hydride. In line with previous results, when (IIIc) was heated with nitrobenzene and a mixture of acetic and hydrochloric acids, the ketone (VIc) was produced in 75% yield.

Condensation of the oxo-ketal (IIa) with ethyl formate in the presence of sodium ethoxide afforded the formyl compound (IId) in high yield. This bright yellow substance behaved as a typical β-dicarbonyl compound, dissolving readily in aqueous sodium hydroxide and exhibiting infrared carbonyl absorption at 6·24 and 6·3 μ. Attempted 12-methylation of its potassium salt with methyl iodide was unsuccessful, giving only the retro-aldol product (IIa). Reduction with lithium aluminium hydride gave the diol (IIId), while catalytic hydrogenation stopped after the uptake of 1 mol. of hydrogen, with the formation of the 12-hydroxymethyl-11-ketone (IIe). The reaction of the diol (IIId) with acids was studied in the expectation that double dehydration would occur to provide an alternative route to (VIc). When the diol was boiled with acetic and hydrochloric acids this compound was indeed formed as the main product (45%). However, when the reaction was conducted in the presence of an excess of nitrobenzene, a second major product, $C_{36}H_{26}O_3$, was isolated in addition to (VIc). This showed a single aryl ketone infrared band, and its ultraviolet spectrum was almost identical with that of (VIc). It is therefore assigned the dimeric ether structure (XVI), and its formation is considered to involve the carbonium ion (XV). In the absence of an oxidising agent, a prototropic shift from C-14 in the initially formed ion (XIV), followed by bond rearrangement and the expulsion of a proton, leads to (VIc). In the presence of nitrobenzene, rapid abstraction of a hydride ion from C-14 in (XIV) leads, by the previously discussed mechanism, to the relatively stable ion (XV) which then attacks a second molecule of hydroxymethyl compound to give (XVI).

Treatment of the oxo-ketal (IIa) with an excess of methylmagnesium iodide, followed by chromatography of the product on alumina, gave two substances, identified by spectroscopy as the 11-methyl-11-en-17-one and its ethylenedioxy-derivative. By heating these with nitrobenzene and acid as usual, the ketone (VId) was formed in 69% yield.

For the preparation of the dimethyl compound (VIe), the methyl-oxo-ketal (IIc) was treated with methyllithium, and the crude product heated with nitrobenzene and acid. Chromatography of the reaction product then furnished the ketone (VIe) in 72% yield, together with a small amount of a compound $C_{19}H_{18}O$. The structure (XI) is assigned to the latter on the following grounds.



The ultraviolet spectrum showed, in addition to maxima at 271 and 281 mμ characteristic of the unconjugated naphthalene chromophore, strong absorption at 255 mμ. The latter was attributed to the αβ-unsaturated ketone which was also indicated by strong infrared bands at 5·88 (conjugated C=O) and 6·1 μ (conjugated double bond, intensity enhanced by *cis* configuration). The n.m.r. spectrum confirmed this structure, with two 3-proton doublets at τ 8·63 (J = 8 c./sec.; secondary 11-methyl group) and at 7·55 (J = 3 c./sec.; 12-methyl group, adjacent to double bond). As expected, (XI) resisted hydrogenation over palladised charcoal; with Adams catalyst, rapid reduction of the ketone was accompanied by disappearance of the 255 mμ absorption band and followed by very slow saturation of the tetrasubstituted double bond without further change in the ultraviolet spectrum.

The ketal (Xb) was also treated with nitrobenzene and acetic–hydrochloric acid in the expectation that (VIe) would be formed through dehydration accompanied by a 1,2-shift of a methyl group to C-11. Compound (VIe) was, in fact, obtained in low yield on prolonged heating, but a product formed in larger amount was a ketone (XII), $C_{19}H_{18}O$, isomeric with (XI). The ultraviolet spectrum of this compound was closely similar to that of 11,12-dihydro-(IX). In addition, the non-aromatic region of the n.m.r. spectrum consisted of a 6-proton singlet at τ 8·68 (two geminal methyl groups) and a 2-proton singlet at 6·86 (benzylic methylene group adjacent to a quaternary carbon atom), together with asymmetrical multiplets at approximately 7·1 and 7·3 arising from the C-15 and C-16 methylene groups, respectively. The equivalence of the two methyl groups indicates that rapid inversion occurs at C-11 and at C-12. The fact that the dihydro-ketones (XI) and (XII), in which enolisation cannot occur towards the C-13 bridgehead, are not further dehydrogenated by nitrobenzene in acetic–hydrochloric acid provides further support for the mechanism proposed above for this aromatisation. The formation of these compounds as by-products in reactions leading to (VIe) probably reflects the strain introduced by steric compression of the methyl groups in the intermediate 11,12-dimethyl-11-ene. That this strain persists in (VIe) is demonstrated by the relative shielding of the methyl resonance in this compound with that in both the 11- and 12-methyl compounds. Cross and Durham[8] recently reported that in 15,16-dihydro-3-hydroxy-1,17,17-trimethylcyclopenta[*a*]phenanthrene absorption of the protons of the 1-methyl group, which is sterically equivalent to the 11-methyl group in (VId), also occurs at τ 7·00, and they attribute this low-field absorption to strong deshielding by all three proximate aromatic rings. The methylene protons are assigned to the 15- and 16-positions as shown by analogy with those in (IX). This compound exhibits two multiplets in the methylene region, at τ 6·85 and 7·75, the areas of which are in the ratio 2 : 1. It therefore follows that the lower figure is associated with the magnetically near-equivalent C-15 and C-17 protons, while the C-16 protons absorb at τ 7·75.

TABLE 1

N.m.r. spectra (τ-values) of 17-oxocyclopenta-[*a*]phenanthrenes (VI)

		CH$_2$ protons		Me protons
		C-15	C-16	
(VIa)	......	6·72t	7·3m	—
(VIc)	......	6·72t	7·3m *	7·18s(3H)
(VId)	......	6·77t	7·32m	7·00s(3H)
(VIe)	......	6·83t	7·3m *	7·25s(6H)

s = singlet, t = triplet, m = multiplet.

* Partly obscured by methyl singlet.

TABLE 2

Infrared and ultraviolet absorption maxima of 17-oxocyclopenta[*a*]phenanthrenes (VI)

	$\nu_{max.}$ (μ)
(VIa)	5·92 (C=O), 11·48, 11·82, 12·40, 12·86, 13·22, 14·18
(VIb)	5·92 (C=O), 11·42, 12·38, 13·04
(VIc)	5·92 (C=O), 11·36, 12·32, 12·70, 13·20
(VId)	5·92 (C=O), 11·40, 12·28, 13·34, 14·00, 14·52
(VIe)	5·94 (C=O), 11·40, 12·38, 13·26, 14·00
(VIf) *	5·88 (C=O), 11·30, 12·30, 13·32
	$\lambda_{max.}$ (mμ) (log ε)
(VIa)	218(4·18), 265(4·89), 284(4·52), 296(4·38), 334(3·24), 350(3·40), 367(3·44)
(VIb)	218—220(4·21), 269sh(4·78), 277(4·83), 319(4·22), 347sh(3·62), 366(3·28),
(VIc)	219(4·18), 268(4·85), 286(4·42), 299(4·36), 340(2·96), 355(3·22), 373(3·28)
(VId)	222(4·11), 264(4·83), 288(4·49), 301(4·32), 342(3·11), 358(3·38), 376(3·43)
(VIe)	218(4·09), 268(4·88), 292(4·45), 304(4·32), 349(3·05), 366(3·34), 383(3·40)
(VIf) *	214(4·21), 261(4·86), 292(4·42), 303(4·29), 346(3·42), 363(3·72), 381(3·82)

* M. p. 184°; prepared according to R. Robinson, *J. Chem. Soc.*, 1938, 1390.

The ultraviolet and infrared absorption maxima of the ketones (VIa—e) and the 11-methoxy-derivative (VIf) are in Table 2. Introduction of a 12-methyl group produces the expected small bathochromic shift of the maximum, but the 11-methyl and 11-methoxy-ketones appear to be anomalous in this respect.

EXPERIMENTAL

Thin-layer chromatograpny (t.l.c.) was carried out using plates coated with silica gel (Merck, Kieselgel G) and dried

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[8] A. D. Cross and L. J. Durham, *J. Org. Chem.*, 1965, **30**, 3199.

overnight in air. Melting points were determined mostly on a hot-stage apparatus. Solutions were dried over anhydrous sodium sulphate. Ether refers to AnalaR diethyl ether, and silica gel was the MFC grade supplied by Hopkin and Williams. Ultraviolet spectra (log ε in parentheses) were recorded for ethanol solutions using a Perkin-Elmer 137UV instrument. Infrared spectra were recorded on a Perkin-Elmer 137 Infracord, and refer to Nujol mulls unless otherwise stated. N.m.r. spectra were recorded on a Varian A60 spectrometer for deuteriochloroform solutions with tetramethylsilane as internal standard.

17,17-*Ethylenedioxy*-11,12,13,14,15,16-*hexahydro*-11-*oxocyclopenta*[a]*phenanthrene* (IIa).—The diketone (Ia) (46·1 g.), m. p. 120° (lit.,[3] 115°), $\lambda_{max.}$ 216 (4·61), 248 (4·33), 315 (3·82) mμ, $\nu_{max.}$ 5·78, 5·98 μ, was heated under reflux with ethylmethyldioxolan (220 ml.; b. p. 117—118°) and toluene-*p*-sulphonic acid (100 mg.) using a short fractionating column equipped with a take-off head. The volatile products were very slowly distilled off through the side-arm, and small amounts of fresh catalyst were added from time to time. After about 20 hr. the temperature of the vapour was constant at 117°. The reaction mixture was cooled, extracted with sodium hydrogen carbonate solution, washed with water, and dried. After removal of the excess of the dioxolan *in vacuo*, the brown gum was crystallised from benzene (60 ml.) and hexane (60 ml.), giving a first crop of crystals (31·9 g.), m. p. 93—95°, and a second crop (11·3 g.), m. p. 84—90°, of less pure material. The *compound* (IIa) crystallised from ethanol in prisms, m. p. 98° (Found: C, 77·85; H, 6·25. $C_{19}H_{18}O$ requires C, 77·5; H, 6·15%), $\lambda_{max.}$ 216 (4·58), 245 (4·31), 313 (3·81) mμ, $\nu_{max.}$ 6·05 μ. The *bisethylenedioxy-compound* (IVa) was also isolated by fractional crystallisation from the products of a reaction in which the heating had been prolonged. This compound, m. p. 170° (from ethanol) (Found: C, 74·5; H, 6·8. $C_{20}H_{21}O_4$ requires C, 74·35; H, 6·55%), $\lambda_{max.}$ 229 (4·92), 280 (3·75) mμ, showed no carbonyl absorption in the infrared. When (IVa) (3·5 g.) was shaken for 3 min. with chloroform (50 ml.) containing 5 drops of conc. hydrochloric acid and worked up as before, (IIa) (1·95 g.), m. p. 95°, was recovered.

17,17-*Ethylenedioxy*-11,12,13,14,15,16-*hexahydro*-3-*methoxy*-11-*oxocyclopenta*[a]*phenanthrene* (IIb).—The diketone (Ib) (10·8 g.), m. p. 133° (lit.,[3] 126—127°), $\lambda_{max.}$ 221 (4·60), 249 (4·32), 315 (3·72) mμ, $\nu_{max.}$ 5·8, 6·0 μ, was treated with ethylmethyldioxolan as described above. Fractional crystallisation of the product from ethanol–ether afforded the *derivative* (IIb) (4·0 g.), m. p. 114° (from ethanol) (Found: C, 74·3; H, 6·1. $C_{20}H_{20}O_4$ requires C, 74·0; H, 6·2%), $\lambda_{max.}$ 221 (4·65), 246 (4·49), 310 (3·76) mμ, $\nu_{max.}$ 6·0 μ, together with the *bisethylenedioxy-compound* (IVb) (3·8 g.), m. p. 174° (Found: C, 71·35; H, 6·7. $C_{22}H_{24}O_5$ requires C, 71·7; H, 6·55%). When (IVb) (2·68 g.) was shaken with chloroform containing hydrochloric acid as before, crystallisation of the crude product from ethanol furnished (IIb) (1·96 g.), m. p. 108°.

Methylation of the Oxo-ketal (IIa).—The oxo-ketal (IIa) (20·25 g.) was boiled under reflux for 15 min. with t-butyl alcohol (640 ml.) containing potassium (8·06 g., 3 equiv.) under an atmosphere of pure, dry nitrogen. After being cooled to 25°, methyl iodide (13 ml., 3 mol.) was added in one lot with vigorous stirring, and cooling was maintained so that the temperature of the mixture did not rise above 27°. After being kept at room temp. for 5 hr., the mixture was poured into water (1·5 l.) and extracted with ether (total, 1 l.). The extracts were washed with water, dried, and evaporated, to give a brown syrup (22 g.) which was chromatographed on a column of alumina (1 kg.); 100-ml. fractions were collected. Fractions 17—41 (ether) were combined (14·56 g.); crystallisation from a mixture of benzene (20 ml.) and hexane (30 ml.) yielded the *methyl-oxo-ketal* (IIc) (11 g.), m. p. 120—121°. A specimen sublimed at 120°/10^{-4} mm. had m. p. 123—124° (Found: C, 77·6; H, 6·5. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·55%), $\lambda_{max.}$ 217 (4·61), 240sh (4·32), 310 (3·81) mμ, $\nu_{max.}$ 6·0 μ. Fractions 46—78 (ether) (2·3 g.), on recrystallisation from hexane, gave the starting material (IIa) (2 g.), m. p. 93—94°. Fractions 11—15 (1 : 1 ether–hexane) crystallised from hexane to yield the *dimethyl-oxo-ketal* (Xa) (1·45 g.), m. p. 162—164°. After two recrystallisations this substance had m. p. 167°, $\lambda_{max.}$ 217 (4·35), 244 (4·14), 306 (3·59) mμ, $\nu_{max.}$ 5·94 μ; a correct analysis was obtained only after sublimation at 150°/10^{-4} mm. although this did not alter this m. p. (Found: C, 78·2; H, 6·85. $C_{21}H_{22}O_3$ requires C, 78·2; H, 6·9%). Rechromatography of fraction 16 (0·93 g.) and various mother-liquor residues (3·58 g.) afforded additional (IIc) (2·1 g.) and (Xa) (0·24 g.). The yield of (IIc) (61·7%) was lower when less than 3 mol. of potassium butoxide and methyl iodide were employed; correspondingly more starting material was recovered. The amount of (Xa) increased at the expense of (IIc) with molar ratios greater than 3.

17,17-*Ethylenedioxy*-12-*formyl*-11,12,13,14,15,16-*hexahydro*-11-*oxocyclopenta*[a]*phenanthrene* (IId).—To methanol-free sodium methoxide (from 0·5 g. of sodium) was added the oxo-ketal (IIa) (2·94 g.), ethyl formate (1·61 ml.), and dry benzene (15 ml.). The flask was filled with dry nitrogen, sealed, and set aside at room temperature for 48 hr. Water was added to dissolve the yellow solid which filled the liquid, and the deep yellow aqueous solution was extracted once with ether. The solution was brought to pH 7·5 by the cautious addition of dilute acetic acid, and the yellow precipitate was collected, dried, and crystallised from hot n-butanol. The *formyl derivative* (IId) was obtained as large yellow prisms (2·74 g.), m. p. 144—145° (Found: C, 74·45; H, 5·75. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·65%), $\lambda_{max.}$ 218 (4·54), 254·5 (4·13), 362 (3·87) mμ, $\nu_{max.}$ 6·24, 6·3 μ.

For attempted methylation, (IId) (1·07 g., 3 mmoles) was heated with t-butyl alcohol (30 ml.) containing potassium (0·375 g.). To the bright yellow suspension of the potassium salt was added methyl iodide (1·42 g., 10 mmoles), and the mixture was boiled gently for 22 hr. The almost colourless solution containing pale fawn solid was poured into water and extracted with ether. Evaporation of the dried extract left a brown syrup (1 g.) which on crystallisation from hexane (30 ml.) gave the unmethylated oxo-ketal (IIa) (0·68 g.), m. p. and mixed m. p. 96—98°.

15,16-*Dihydro*-17-*oxocyclopenta*[a]*phenanthrene* (VIa).—*By the general procedure.* The oxo-ketal (IIa) (6·2 g.), tetrahydrofuran (40 ml.), water (10 ml.), and sodium borohydride (2 g.) were heated under reflux with stirring for 5 hr., then left at room temp. for 20 hr. The excess of reducing agent was destroyed by the careful addition of dilute acetic acid to bring the pH to 6·5, and, after the addition of more water, the mixture was extracted with ether, the extract was washed with sodium hydrogen carbonate solution and water, and dried. Removal of the solvent left a semi-crystalline mass (6·15 g.) which showed no infrared carbonyl absorption.

This material was dissolved in a mixture of glacial acetic acid (120 ml.) and nitrobenzene (30 ml.); addition of conc. hydrochloric acid (30 ml.) produced a green coloration which became yellow-brown after being heated for a few minutes. Heating under reflux was continued for 30 min., the mixture was diluted with water, and the nitrobenzene was removed by distillation in steam. When cold, the brown solid was dried (4·2 g., 85·8%), m. p. 197°. Recrystallisation from benzene (150 ml.; charcoal) yielded the ketone (VIa) as very pale yellow needles (3·6 g.), m. p. 203—204° (lit.,[9] 200—201°) (Found: C, 87·8; H, 5·2. Calc. for $C_{17}H_{12}O$: C, 87·9; H, 5·2%).

By the general procedure, but with omission of nitrobenzene. The oxo-ketal (IIa) (1·0 g.) was reduced with sodium borohydride as described above. The product was dissolved in acetic acid (80 ml.) and boiled for 1 hr. with conc. hydrochloric acid (20 ml.), to give a yellow solution. After removal of the solvent *in vacuo* the residue was dissolved in benzene (20 ml.) and chromatographed on alumina (90 g.). The initial fractions, eluted with 0·1% methanol in benzene and together weighing 148 mg., were recrystallised from light petroleum (b. p. 60—80°) (20 ml.), to give the ketone (VII) (88 mg.), m. p. 115° (lit.,[3] 111—112°) (Found: C, 86·45; H, 6·85. Calc. for $C_{17}H_{16}O$: C, 86·4; H, 6·85%), $\lambda_{max.}$ 228 (5·92), 280 (3·82) mμ, $\nu_{max.}$ 5·8 μ. Later fractions (513 mg., eluted with 0·3% methanol in benzene) were recrystallised from benzene, to furnish (VIa) (273 mg.), m. p. 201—202°.

15,16-*Dihydro*-3-*methoxy*-17-*oxocyclopenta*[a]*phenanthrene* (VIb).—The methoxy-oxo-ketal (IIb) (5·65 g.) was submitted to the general procedure described above. The crude product (4·8 g.), m. p. 192—197°, crystallised from benzene (200 ml., charcoal), to give the *methoxy-ketone* (VIb) (3·83 g., 83·7%), m. p. 208—214°; the analytical sample showed a double m. p. at 209 and 230° (Found: C, 82·7; H, 5·2. $C_{18}H_{14}O_2$ requires C, 82·5; H, 5·4%).

Treatment of 11,12,13,14,15,16-*Hexahydro*-11,17-*dihydroxy*-15H-*cyclopenta*[a]*phenanthrene with Nitrobenzene and Acid.*—The diketone (Ia) (5·0 g.) was reduced with sodium borohydride (5·0 g.) in tetrahydrofuran (100 ml.) and water (20 ml.) for 17 hr. under reflux. The pale yellow solution was poured into water (600 ml.), acidified with 2N-hydrochloric acid, and the gum extracted with ether. On evaporation, the dried solution yielded a glassy solid (5·1 g.) which lacked infrared carbonyl absorption.

This diol was treated with nitrobenzene and acid by the general procedure. After removal of the nitrobenzene by distillation in steam, the brown oil was extracted with ether, and the solution washed, dried, and evaporated, to give an oil which exhibited strong infrared ester absorption at 5·8 and 8·1 μ. It was saponified with sodium hydroxide (5·0 g.), in methanol (150 ml.) and water (10 ml.), for 45 min. under reflux. The hot solution was decanted from some dark resinous material (0·5 g.), poured into water (500 ml.), and extracted with ether. The dark gum, obtained on removal of the solvent from the dried extract, was chromatographed on alumina (Wöelm, Brockmann Grade 1; 300 g.) with benzene containing increasing proportions of methanol. The first few fractions yielded an oil which crystallised (320 mg.) (A). A small amount of a mixture consisting of two substances (t.l.c.) was eluted with 1% methanol in benzene, but was not further investigated. The main fraction, a brown gum (3·455 g.) (B), was eluted with 1—1·5% methanol in benzene; only a trace of material was obtained on further elution (up to 2% of methanol). Fraction A was shown by t.l.c. (4 : 1 hexane–benzene) to consist of two substances, R_F 0·85 and 0·77, both of which gave blue spots after being heated with sulphuric acid. Identical spots were given by compound (IX) and the 15,16-dehydro-derivative,* respectively. Recrystallisation of A from methanol (15 ml.) gave crystals (85 mg.), m. p. 127—130°, of (IX) contaminated with a small amount of the 15-ene (t.l.c.). Fraction B was crystallised from ethanol (10 ml.) from which separated the *hydroxy-compound* (Vb) (1·468 g.), m. p. 117—118° (Found: C, 86·1; H, 7·0. $C_{17}H_{16}O$ requires C, 86·4; H, 6·85%), $\lambda_{max.}$ 239 (4·75), 301·5 (3·85), 315 (3·95), 330 (3·79), 336 (3·69) mμ, $\nu_{max.}$ 3·0 and 9·35 μ (OH). T.l.c. (dichloromethane) of the mother-liquor revealed four spots, R_F 0·60, 0·44, 0·31 (Vb), and 0·21; the last, blue with sulphuric acid, was identical with that given by a sample of 15,16-dihydro-17-hydroxycyclopenta[*a*]phenanthrene * prepared by reduction of the 17-ketone with sodium borohydride.

The unsaturated alcohol (Vb) (229 mg.) was hydrogenated in ethyl acetate with Adams catalyst (10 mg.). When the calculated volume of hydrogen had been consumed (15 min.), the solution was filtered free from catalyst and evaporated to give a crystalline mass, $\lambda_{max.}$ 280 mμ. The crystals were dissolved in acetone (10 ml.), and an aqueous solution (0·5 ml.) of chromic acid [from potassium dichromate (5·0 g.) and 96% sulphuric acid (3·75 ml.) made up to 25 ml. with water] was added dropwise. After 15 min. at room temperature, the mixture was diluted with water and extracted with ether, and the solution was washed, dried, and evaporated, to leave a crystalline residue (220 mg.). Recrystallisation from hexane (40 ml.) afforded the ketone (VII) as rosettes of needles, m. p. 114—114·5° alone and when mixed with the analytical specimen.

The unsaturated alcohol (Vb) (1·10 g.) was kept at 40° with a mixture of chromium trioxide (3·0 g.) and pyridine (90 ml.) for 22 hr. After dilution with water and addition of an excess of sodium pyrosulphite, the solution was extracted with dichloromethane. The extract was washed with dilute sulphuric acid, aqueous sodium hydrogen carbonate, and water, and dried. Evaporation of the solvent left a pale brown solid which was recrystallised from benzene to afford (VIa) (0·74 g., 68%), m. p. and mixed m. p. 202°. T.l.c. revealed minor amounts of several other substances in the mother-liquor.

Oxidation of (Vb) (240 mg.) with chromic acid in acetone, essentially as described above for the saturated alcohol, gave a product which was shown to consist of at least eight substances by t.l.c. Careful column chromatography on silica gel with hexane–dichloromethane (2 : 1) gave a chromatographically homogeneous fraction (42 mg.), $\lambda_{max.}$ 316 mμ, which, on crystallisation from hexane, yielded (Va) (10 mg.), m. p. 96—98°, the infrared and ultraviolet spectra of which were identical with those of the analytical sample described below.

13,14,15,16-*Tetrahydro*-17-*oxocyclopenta*[a]*phenanthrene* (Va).—The hydroxy-ketal (IIIa) (2·5 g.) in dry pyridine (6 ml.) was allowed to stand at room temp. for 72 hr. with toluene-*p*-sulphonyl chloride (1·8 g.). After dilution with saturated sodium chloride solution (200 ml.) and extraction with dichloromethane, the crude tosylate was obtained as a brown gum (3·7 g.) by evaporation of the solvents. This material was boiled for 1 hr. with redistilled collidine

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* See Part II (following Paper).

[9] D. Nasipuri and D. N. Roy, *J. Chem. Soc.*, 1961, 3361.

(10 ml.). The cooled solution was diluted with ether (200 ml.) and quickly extracted with N-hydrochloric acid (200 ml.) and with sodium hydrogen carbonate solution, and dried. Removal of the solvent under reduced pressure left a crystalline solid (2·2 g.) which on recrystallisation from ethanol furnished cream prisms (1·12 g.), m. p. 92—95°. The *ethylenedioxy-compound* (Vc) formed leaflets (from ethanol), m. p. 96° (Found: C, 82·0; H, 6·65. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%), $\lambda_{max.}$ 239 (4·81), 302 (3·89), 314 (4·00), 319 (3·84), and 336 (3·72) mμ.

This ketal (250 mg.) was dissolved in tetrahydrofuran (25 ml.) containing 5N-hydrochloric acid (0·8 ml.). After 8 hr. at room temp. the mixture was diluted with water (100 ml.), extracted with ether, and the extract washed with aqueous sodium hydrogen carbonate. Chromatography of the semi-solid residue (obtained by concentration of the dried extract) on silica gel with hexane–dichloromethane (2 : 1) gave a crystalline solid (144 mg.), m. p. 85—90°, recrystallisation of which from hexane afforded the *ketone* (Va) (48 mg.), m. p. 95—96° (Found: C, 87·35; H, 6·45. $C_{17}H_{14}O$ requires C, 87·15; H, 6·0%), $\lambda_{max.}$ 239 (4·73), 303 (3·88), 316 (4·01), 330 (3·88), and 336 (3·86) mμ, $\nu_{max.}$ 5·75 μ (unconjugated C=O). In preliminary small-scale experiments this hydrolysis was monitored by t.l.c. When hydrolysis of the ketal was almost complete (about 8 hr.) formation of (VIa) was already appreciable, and after 30 hr. the ketone (Va) was practically all converted into (VIa) and two other substances less polar than (VIa).

Treatment of the Unsaturated Ketal (Vc) *with Acetic and Hydrochloric Acids.—In the presence of nitrobenzene.* The unsaturated ketal (Vc) (278 mg.) was dissolved in a mixture of acetic acid (5 ml.) and nitrobenzene (1 ml.), and boiled for 30 min. with concentrated hydrochloric acid (1 ml.). The mixture was diluted with water, the nitrobenzene removed in steam, and, when cold, the pale brown crystalline deposit of pure (VIa) (211 mg., 91%), m. p. 202—204°, collected and dried.

In the absence of nitrobenzene. The above experiment was repeated without the addition of nitrobenzene. The deep orange solution was diluted with water, extracted with dichloromethane, and the extracts were washed with sodium hydrogen carbonate solution and dried. Evaporation left a yellow gum (236 mg.) which was chromatographed on silica gel in dichloromethane. The first fractions yielded (VII) (85 mg.), m. p. 103—108° (109—112° when mixed with an authentic specimen of m. p. 114—115°). Further elution gave (VIa) (100 mg.), m. p. 198—201°. Elution of the column with 1% ethanol in dichloromethane then afforded pale yellow leaflets (50 mg.) of the 11,12-dihydro-derivative of (VIa), m. p. 219—221° (lit.,[5] 222·5—223·3°) (Found: C, 87·35; H, 6·15. Calc. for $C_{17}H_{14}O$: C, 87·15; H, 6·0%), $\lambda_{max.}$ 219 (4·59), 242 (3·80), 251sh (4·25), 271 (4·59), 281 (4·69), 326 (4·10), 338 (4·14), and 362sh (3·93) mμ (lit.,[6]), $\nu_{max.}$ 5·92 (conjugated C=O), 6·1 μ (conjugated C=C).

Dehydration–dehydrogenation Experiments with the 11-*Hydroxy-compound* (VIIIb).— The ketone (VIIIa) (1·0 g.), m. p. 115—117°, prepared according to Dannenberg,[7] was reduced with sodium borohydride in the usual way to form the 11-ol (VIIIb) (0·98 g.), $\lambda_{max.}$ 229 and 283 mμ, no carbonyl absorption in the infrared.

This alcohol (0·50 g.), in glacial acetic acid (10 ml.) and nitrobenzene (2·5 ml.), was boiled for 30 min. with concentrated hydrochloric acid (2·5 ml.). After dilution with water the nitrobenzene was removed in steam, and the gum which had separated was extracted with ether. Evaporation of the washed and dried extracts gave an amber gum which showed 10 spots on a thin-film plate. The gum was placed on a column of alumina (80 g.; Wöelm, Grade I, neutral), and the following were eluted, in this order, with hexane: compound (VIIIc) (73 mg.), m. p. 85—87°; *compound* (Vd) (14 mg.), m. p. 73—75°; compound (IX) (100 mg.), m. p. 108—117°.

When this reaction was repeated (0·48 g. of VIIIb) without nitrobenzene, the product appeared identical with that above by t.l.c., and the same three compounds were obtained: (VIIIc) (68 mg.), m. p. 87—89°; (Vd) (46 mg.), m. p. 72—75°; (IX) (103 mg.), m. p. 110—120°.

Recrystallisation of (VIIIc) (from both experiments, total was 141 mg.) from ethanol gave needles (84 mg.), m. p. 91—92°, not raised by further recrystallisation (lit.,[10] 85—87°) (Found: C, 91·65; H, 8·25. Calc. for $C_{17}H_{18}$: C, 91·85; H, 8·15%), $\lambda_{max.}$ 230 (4·28), 275 (3·63), 285 (3·76), and 292 (3·54) mμ.

Recrystallisation of (Vd) (total, 60 mg.) from ethanol followed by sublimation at 100°/10^{-5} mm. yielded the *hydrocarbon*, m. p. 79—80° (Found: C, 92·5; H, 7·5. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%), $\lambda_{max.}$ 239 (4·76), 303 (3·84), 315 (3·91), and 337 (3·63) mμ, $\nu_{max.}$ 10·55, 11·54, 12·15, 12·42, 13·25, 13·5, and 13·8 μ.

The infrared and ultraviolet spectra of (IX) from both experiments were identical with those of a pure sample.

15,16-*Dihydro*-12-*methyl*-17-*oxocyclopenta*[a]*phenanthrene* (VIc).—*By the general procedure.* The methyl-oxo-ketal (IIc) (3·0 g.) in tetrahydrofuran (90 ml.) was reduced by the addition of lithium aluminium hydride (3·0 g.) in small portions with stirring during 3 hr. at room temperature, and the mixture was left overnight. Excess of hydride was destroyed by the cautious addition of ethyl acetate, and the mixture was diluted with water and brought to pH 7 with 2N-acetic acid. The reduction product was extracted with ether and the extract was washed and dried. Evaporation of the solvent left a gum (2·37 g.) devoid of infrared carbonyl absorption. Treatment of this with nitrobenzene and acid by the general procedure gave the *methyl-ketone* (VIc) (1·80 g., 75%), m. p. 233° (from benzene) (Found: C, 88·1; H, 5·65. $C_{18}H_{14}O$ requires C, 87·75; H, 5·75%).

From the 12-*formyl compound* (IId). (*a*) The formyl compound (966 mg.) was suspended in ethanol (40 ml.) and shaken in hydrogen with Adams catalyst (100 mg.). Uptake of hydrogen was rapid at first, but became very slow. After filtration from the catalyst, the solution was evaporated, leaving a pale yellow gum, $\lambda_{max.}$ 307 (3·93) mμ, $\nu_{max.}$ 2·94 (OH) and 5·96 μ (11-carbonyl), which was reduced with lithium aluminium hydride (500 mg.) in tetrahydrofuran (10 ml.) as previously described. Infrared carbonyl absorption was virtually absent from the spectrum of the product (842 mg.). Treatment of the latter with nitrobenzene and acid by the general procedure gave a dark brown solid (656 mg.), t.l.c. (1 : 1 dichloromethane–benzene) of which revealed (VIc) (R_F 0·44) and a second major product (R_F 0·50), together with several less polar spots. Fractional crystallisation from benzene afforded (VIc) (51 mg.), m. p. 208—213° (infrared spectrum identical with that of the authentic material) and the R_F 0·5 material, *di*-(15,16-*dihydro*-17-*oxocyclopenta*[a]*phenanthr*-12-*ylmethyl*) *ether* (XVI) (70 mg.), m. p. 229—233° (Found: C, 85·55; H, 5·15%; *M*, 510. $C_{36}H_{26}O_3$ requires C, 85·35; H, 5·15%;

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[10] E. Bucha and H. Ziemer, *Annalen*, 1956, **601**, 155.

M, 506·6), $\lambda_{\text{max.}}$ 219, 267·5, 286, 298, 338, 353, 371 mμ, $\nu_{\text{max.}}$ 5·92 (C=O), 12·32, 13·36, 13·68, 14·50 μ.

(*b*) The formyl compound (500 mg.) was reduced with lithium aluminium hydride (500 mg.) in tetrahydrofuran (10 ml.) under gentle reflux for 8 hr. and worked up as before to give an amber gum (377 mg.), the infrared spectrum of which was identical with that of the 842 mg. (above). This gum was dissolved in glacial acetic acid (10 ml.) and boiled with conc. hydrochloric acid (2·5 ml.) for 30 min. After dilution with water, the mixture was extracted with dichloromethane, and the extract washed and dried as usual, and evaporated; t.l.c. demonstrated the absence of products less polar than (VIc) in the residue. Chromatography of the resinous product on alumina (50 g.) with 2 : 1 dichloromethane–benzene, furnished (VIc) (171 mg., 45%), m. p. 230°.

15,16-*Dihydro*-11-*methyl*-17-*oxocyclopenta*[a]*phenanthrene* (VId).—To a solution of methylmagnesium iodide [from magnesium (0·61 g.), methyl iodide (4 g.), and ether (50 ml.)] was added a solution of the oxo-ketal (IIa) (5·88 g.) in ether (120 ml.) and benzene (20 ml.) under nitrogen. The mixture was stirred and boiled gently under reflux for 4 hr., then set aside at room temperature overnight. The reaction mixture was shaken with ice-cold ammonium chloride solution, and the organic layer separated, washed with water, and dried. The residue (6·1 g.), obtained on evaporation of the solvents and still containing some unchanged 11-ketone (weak $\nu_{\text{max.}}$ 6·0 μ), was chromatographed on alumina. Two main fractions, together weighing 3·54 g. and probably consisting of the Δ^{11}-11-methyl-17-ketone ($\lambda_{\text{max.}}$ 318 mμ, $\nu_{\text{max.}}$ 5·8 μ) and the corresponding 17,17-ethylenedioxy-compound ($\lambda_{\text{max.}}$ 318 mμ, no infrared carbonyl absorption), were eluted with benzene containing 0·1—0·5% of ethanol. This material (3·54 g.) was treated with nitrobenzene and acid by the general procedure, to afford the *methyl-ketone* (VId) as pale yellow needles (from ethyl acetate) (2·32 g., 69·2% based on the isolated intermediates; 47·2% overall), m. p. 171—172° (Found: C, 88·0; H, 5·55%). The overall yield was 50% when the crude product of the Grignard reaction was heated with nitrobenzene and acid without previous purification.

15,16-*Dihydro*-11,12-*dimethyl*-17-*oxocyclopenta*[a]*phenanthrene* (VIe).—*From the* 12-*methyl-oxo-ketal* (IIc). To a freshly prepared solution of methyl-lithium [from lithium chips (3·6 g.), methyl iodide (20 ml.), and ether (500 ml.)] was added a solution of (IIc) (4·20 g.) in benzene (20 ml.), with stirring under nitrogen. When the addition was complete, the mixture was boiled under reflux for 5 hr., and left at room temperature overnight. The mixture was decomposed with ice, and the organic layer dried and evaporated, to yield a brown gum which exhibited weak 11-ketone absorption at 5·95 μ. This was heated with nitrobenzene and acid by the general procedure; the initial deep green coloration gradually became dark brown, and heating was continued for 1 hr. The brown oil which remained after steam-distillation was extracted with dichloromethane, the extract was washed with 5% sodium hydroxide solution, dried, and evaporated, and the residue was chromatographed on alumina (150 g.) with mixtures of hexane and benzene containing increasing proportions of the latter. Later fractions were combined and evaporated, to yield the *dimethyl-ketone* (VIe) (2·57 g., 72%), m. p. 148—149°, raised to 149—150° by one recrystallisation from methanol (360 ml.) (Found: C, 87·65; H, 6·0. $C_{19}H_{16}O$ requires C, 87·65; H, 6·2%). Earlier fractions from the column were combined and crystallised from ethanol, to furnish cream needles of the *unsaturated dimethyl-ketone* (XI) (424 mg.), m. p. 178° (Found: C, 87·3; H, 7·2. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%), $\lambda_{\text{max.}}$ 228 (5·01), 255 (4·07), 271 (3·86), 281 (3·78) mμ, $\nu_{\text{max.}}$ 5·88 (C=O), 6·1 (C=C), 11·6, 11·8, 12·3, 13·0, 13·4, 13·6 μ. This compound (40 mg.), in ethyl acetate (20 ml.), was not reduced when shaken with 5% palladium–charcoal in an atmosphere of hydrogen. With Adams catalyst (5 mg.), approximately 1 mol. of hydrogen was absorbed in 1 hr.; a portion of the solution, on dilution with ethanol, then showed $\lambda_{\text{max.}}$ 281 mμ. A further 70 hr. was required to complete the uptake of the second mol. of hydrogen, and the ultraviolet spectrum of the product was identical with that of the partially reduced material.

From the dimethyl-oxo-ketal (Xa). This compound (1·33 g.) was reduced with lithium aluminium hydride (0·75 g.) in boiling tetrahydrofuran (20 ml.) for 1·5 hr. and then left at room temperature overnight. The product obtained on working up the solution in the usual way was a yellow resin (1·31 g.), $\nu_{\text{max.}}$ 2·9 μ (OH); no carbonyl absorption.

This alcohol was dissolved in a mixture of acetic acid (40 ml.) and nitrobenzene (10 ml.). Addition of conc. hydrochloric acid (10 ml.) produced a brilliant emerald green solution, the appearance of which was unchanged after being boiled for 0·5 hr. On further heating, the colour gradually became brown, and after 22 hr. a portion showed strong infrared absorption at 5·9 μ (conjugated C=O). The solution was diluted with water, and the brown oil which remained after removal of the nitrobenzene in steam was chromatographed on a column of silica gel (200 g.) with hexane containing increasing concentrations of dichloromethane; 50-ml. fractions were collected. T.l.c. revealed that fractions 75—85 contained almost pure dimethyl-ketone (VIe); evaporation yielded fawn needles (101 mg.) which, after one recrystallisation from ethanol, had m. p. 148—149°. Fractions 86—95 were mixtures and were not further investigated. On evaporation, fractions 96—127 gave brown crystals (180 mg.) which were recrystallised from ethanol to yield 11,12,15,16-*tetrahydro*-12,12-*dimethyl*-17-*oxocyclopenta*[a]*phenanthrene* (XII) as prisms (112 mg.), m. p. 186—187° (Found: C, 86·9; H, 6·8%; *M*, 252. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9%; *M*, 262·3), $\lambda_{\text{max.}}$ 219 (4·87), 241 (4·11), 251sh (4·16), 262sh (4·57), 270 (4·89), 281 (5·00), 324 (4·48), 336 (4·51), 362sh (4·25) mμ, $\nu_{\text{max.}}$ 5·90 (C=O), 10·1, 12·3, 12·78, 13·22 μ.

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