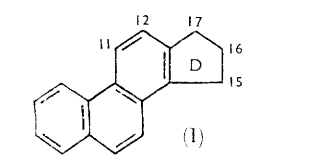
Potentially Carcinogenic Cyclopenta[*a*]phenanthrenes (1,2-Cyclopentenophenanthrenes). Part II.[1] Derivatives Containing Further Unsaturation in Ring D

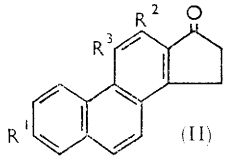
By M. M. Coombs

Substituted 17-methyl-15*H*-cyclopenta[*a*]phenanthrenes have been prepared from the corresponding 15,16-dihydro-17-ketones by the Grignard reaction, and reduced to the analogues of the Diels hydrocarbon. The 15,16-dihydro-17-methylene-derivative (unsubstituted) was obtained by the Wittig reaction. Elimination from the 17-toluene-*p*-sulphonyloxy-compound at 170° gave the Δ^{15} – 17*H*-compound (A), but at 100° the Δ^{16} – 15*H*-isomer was formed. Base-catalysed condensation of (A) with acetone and aryl aldehydes yielded 17-substituted-methylene derivatives. The chemical shifts of protons attached to ring D in these compounds are listed.

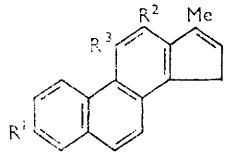
ALTHOUGH 1,2-cyclopentenophenanthrene (16,17-dihydro-15*H*-cyclopenta[*a*]phenanthrene) (I) is not itself carcinogenic, weak activity has been reported for the 11-methyl and 11,12-dimethyl compounds [1] and for derivatives of (I) containing further unsaturation in the D-ring.[2] It was therefore of interest to investigate whether carcinogenic potency would be enhanced by the presence of both of these structural features in the same molecule. The recent demonstration [3] of the presence of 16,17-dihydro-3-hydroxy-15*H*-cyclopenta[*a*]phenanthrene in the pyrolysis products of natural fats makes the study of compounds oxygenated at positions 17, 11, and 3 of particular relevance. The availability of a number of the methyl and methoxy-17-ketones by a new route [4] prompted the present investigation.



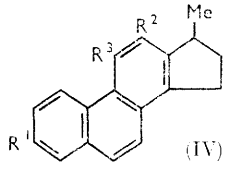
(I)



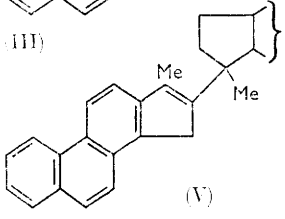
(II)



(III)



(IV)



(V)

	R^1	R^2	R^3
a:	H	H	H
b:	OMe	H	H
c:	H	Me	H
d:	H	H	Me
e:	H	Me	Me
f:	H	H	OMe

Dannenberg *et al.*[5] obtained the 17-methyl compound (IIIa) from the 17-ketone (IIa) by a Grignard reaction followed by chromatography of the crude tertiary alcohol on alumina, and reported the concomitant formation of a dimer, $C_{36}H_{28}$. This has now been confirmed, and the method applied to the ketones (IIb—f) to prepare the corresponding 17-methyl-16-enes (IIIb—f). The yields of the latter varied considerably (see Table 3); since no attempt was made to isolate the dimers [except from the reactions with (IIa) and (IIf)], these yields probably provide a rough indication of the amount of dimer formed. In the case of (IIf), crystallisation of the crude Grignard reaction product from boiling alcohol gave the 11-methoxy-monomer (IIIf) in 85% yield, whereas the yield was only 18% when the crude product was chromatographed in the usual way, and much 11-methoxy-dimer was also isolated. It therefore appears that dimerisation accompanied dehydration on the chromatographic column, although neutral alumina was employed. The structure (V) suggested by Dannenberg for the unsubstituted dimer was confirmed by its nuclear magnetic resonance (n.m.r.) spectrum, which exhibited methyl absorption (total of 6 protons) at τ 8·23 (singlet) and 8·12 (closely spaced doublet, $J = 2$ c./sec.) together with a well-resolved 2-proton multiplet at 6·2 assigned to the C-15 methylene protons adjacent to the 16-double bond. In addition, absence of absorption in the olefinic proton region and absorption in the aromatic proton region closely similar to that of the monomer (IIIa) strengthened this evidence. Hydrogenation of the monomers (IIIb—f) furnished the 17-methyl compounds (IVb—f), derivatives of the Diels hydrocarbon (IVa); the dimer (V) resisted hydrogenation, as expected from the sterically hindered nature of its 16-double bond.

The ultraviolet absorption maxima of these compounds are summarised in Table 1. Conjugation of the 16-double bond causes a bathochromic shift of about 15 mμ in the main peak, and further small shifts are caused by the introduction of methyl substituents into the phenanthrene nucleus. Methyl and methoxy substitution at C-11 is anomalous as noted [4] for the ketones (IId) and (IIf). The moderate-to-weak absorption bands in the 280—380 mμ region are particularly useful for the identification of the compounds in these various series. The strong infrared bands in the 10—15 μ region are also listed in Table 1.

Dannenberg *et al.*[5] reported that, when using the methyl Wittig reagent, the ketone (IIa) gave the 16-ene (IIIa).

* Part I, M. M. Coombs, preceding Paper.

[1] A. Butenandt, H. Dannenberg, and D. von Dresler, *Z. Naturforsch.*, 1946, **1**, 153.

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

[3] K. Hoffelner, H. Libet, and L. Schmidt, *Z. Ernaehrungswiss.*, 1964, **5** (*1*), 16.

[4] Part I; also M. M. Coombs, *Chem. and Ind.*, 1965, 270.

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

TABLE 1

Ultraviolet and infrared absorption maxima of cyclopenta[*a*]phenanthrenes (III) and (IV)

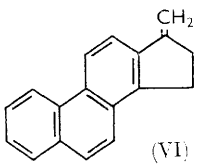
	$\lambda_{max.}$ (mμ) (log ε)
(IIIa)	.....223(4·30), 270(4·70), 276(4·73), 293·5(4·14), 316(3·74), 331(2·71), 348(2·69), 366(2·46)
(IIIb)	.....223(4·28), 273(4·84), 294(4·22), 304sh(4·16), 318(4·10), 338(2·92), 355(3·04), 374(3·03)
(IIIc)	.....222·5(4·38), 272(4·808), 276sh(4·807), 290(4·27), 318(3·88), 349(2·71), 367(2·43)
(IIId)	.....222(4·32), 270(4·70), 276·5(4·81), 295sh(4·13), 306sh (4·13), 317(3·69), 350(2·93), 368(2·83)
(IIIe)	.....219(4·35), 280(4·93), 311(4·14), 355sh(2·78)
(IIIf)	.....221(4·37), 272(4·70), 280(4·74), 287(4·63), 324(3·69), 339(3·29), 356(3·49), 374(3·57)
(IVa)	.....218(4·39), 259(4·69), 280(4·07), 288(3·99), 300(4·05), 320(2·76), 336(2·86), 352(2·87)
(IVb)	.....212(4·42), 225(4·30), 236(4·36), 261(4·82), 282(4·20), 291(4·12), 302(3·95), 326(2·83), 341(3·16), 358(3·28)
(IVc)	.....217(4·63), 261(4·83), 290(4·06), 303(4·13), 321(2·57), 337(2·64), 353(2·41)
(IVd)	.....219(4·45), 227(4·19), 257(4·80), 294(4·02), 306(4·07), 324(2·85), 339(3·00), 355(3·03)
(IVe)	.....218(4·33), 224·9(26), 261(4·71), 287(3·98), 301(3·97), 312(4·01), 343(3·17), 360(3·07)
(IVf)	.....218—220sh(4·42), 228(4·45), 246·5(4·60), 252·5(4·59), 276(4·44), 298(3·95), 330(3·25), 345(3·55), 362(3·65)

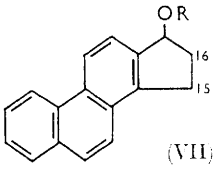
	$\nu_{max.}$ (μ)
(IIIa)	.....11·0, 11·55, 12·0, 12·3, 12·8, 13·4, 13·82
(IIIb)	.....10·94, 11·64, 12·22, 13·1, 13·82
(IIIc)	.....10·96, 11·44, 12·28, 12·34, 13·15, 13·34
(IIId)	.....10·9, 11·52, 12·2, 13·06, 13·32, 13·86
(IIIe)	.....10·9, 12·3, 13·18, 13·34, 13·64, 14·9
(IIIf)	.....10·92, 11·95, 12·1, 12·2, 12·55, 13·1, 13·35, 13·9
(IVa)	.....11·6, 12·06, 12·36, 13·06, 13·4, 13·9
(IVb)	.....11·64, 12·28, 12·45, 13·84
(IVc)	.....11·5, 12·22, 13·42
(IVd)	.....11·4, 12·02, 12·24, 13·28, 13·4, 13·94, 14·6
(IVe)	.....11·5, 12·12, 12·56, 13·3, 13·86
(IVf) *	.....11·92, 12·26, 12·56, 13·3, 13·96

* Liquid film

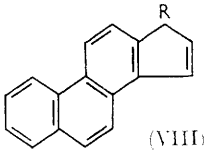
However, in our hands the 17-methylene compound (VI) was isolated without difficulty, but it isomerised to (IIIa) in the presence of traces of acid. The ultraviolet absorption maximum of (VI) (273·5 mμ) was near that of (IIIa) (276 mμ), but in addition (VI) also exhibited a series of weak bands of increasing intensity at 333, 349, and 367 mμ, unlike (IIIa) but similar to those of the ketone (IIa) which also has an exocyclic double bond at C-17. In addition, (VI) showed the expected infrared exocyclic methylene absorption at 3·25 and 6·18 μ, absent from the spectrum of (IIIa). In the n.m.r. spectrum of (VI) signals due to the olefinic protons appeared at τ 4·44 and 4·87 while the C-15 and C-16 methylene protons were represented by multiplets at 6·95 and 6·75. When the spectrum was determined in deuteriochloroform which had not been purified from traces of acid, the spectrum of (IIIa) was observed. This consisted of methyl absorption, a 3-proton doublet (J = 2 c./sec., further split) at 7·7, a 1-proton olefinic peak at 3·55, and a well-resolved 2-proton triplet at 6·34 derived from the C-15 methylene group.

In order to prepare the unknown 15*H*-cyclopenta[*a*]phenanthrene, compound (IIa) was reduced with sodium borohydride to the 17-ol (VIIa) and converted into the tosylate (VIIb). Base-catalysed elimination with boiling collidine then afforded a compound, m. p. 164—165°, in high yield, having the same ultraviolet absorption characteristics as 17*H*-cyclopenta[*a*]phenanthrene reported [6] for a sample of the same m. p. prepared [7]

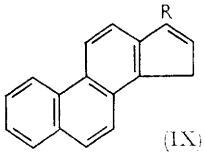

(VI)


(VII)

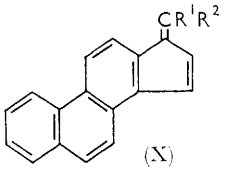
a: R = H
b: R = Tos


(VIII)

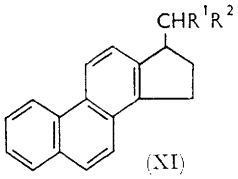
a: R = H
b: R = $CHMe_2$


(IX)

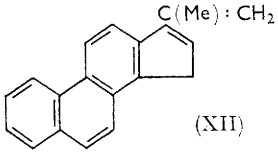
a: R = H
b: R = $CHMe_2$


(X)

a: R^1 = H, R^2 = Ph
b: R^1 = R^2 = Me
c: R^1 = H, R^2 = *p*-$NMe_2 \cdot C_6H_4$


(XI)

a: R^1 = H, R^2 = Ph
b: R^1 = R^2 = Me

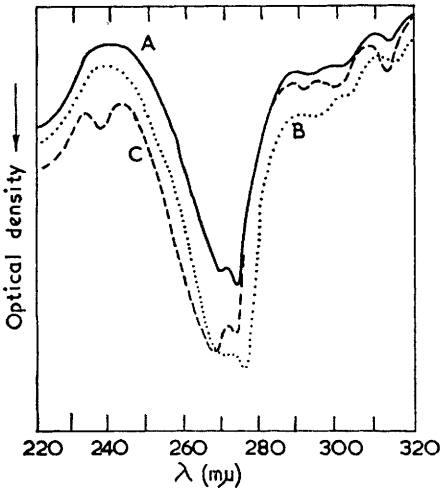

(XII)

through decarboxylation of the 17-carboxylic acid. In particular, it showed the small peak at 240 mμ which was claimed [5] to be diagnostic of the Δ^{15} system. In order to confirm the identity of our compound, 16,17-dihydro-15-oxocyclopenta[*a*]phenanthrene [8] was prepared and reduced with borohydride. Conversion of the 15-ol into its tosylate, and elimination from the latter as before, then furnished the Δ^{15}-compound (VIIIa) identical with this compound derived from the 17-ketone.

An isomeric compound, m. p. 182—183°, obtained by Kon [9] by selenium dehydrogenation of the phosphoric acid cyclisation product of 2-(2-2′-naphthylethyl)cyclopentanol and claimed to be the 15*H*- or 17*H*-compound was shown by Cook and Hewett [10] to be chrysofluorene. Recently Kotlyarevskii and Zanina [11] isolated a compound, m. p. 182—182·5°, from the products of

[6] H. Dannenberg and W. Steidle, *Z. Naturforsch.*, 1954, **9**b, 294.
[7] O. Süss, *Annalen*, 1953, **579**, 133.
[8] W. E. Bachmann and M. C. Kloetzel, *J. Amer. Chem. Soc.*, 1937, **59**, 2207.
[9] G. A. R. Kon, *J. Chem. Soc.*, 1933, 1081.
[10] J. W. Cook and C. I. Hewett, *J. Chem. Soc.*, 1934, 365.
[11] L. Kotlyarevskii and A. S. Zanina, *Zhur. obshchei Khim.*, 1961, **31**, 3206.

pyrolysis of 1-(1,2,3,4-tetrahydro-1-hydroxy-1-naphthyl)-2-(1-hydroxycyclopentyl)acetylene at 400—500° over a magnesia–chromia–alumina catalyst. This was claimed to be a 1,2-cyclopentadienophenanthrene by reference to Kon's original Paper and by the fact that on hydrogenation it consumed 2 atoms of hydrogen to give (I). However, these authors make no reference to the later work of Cook and Hewett. The 15-ene (VIIIa), m. p. 164—165°, obtained in the present work also absorbed 2 atoms of hydrogen to yield (I), but its ultraviolet and infrared spectra differed from those of the Russian compound. It appeared unlikely that the latter was the unkown Δ^{16}-isomer because this must have been formed initially during the elimination of the 17-tosylate, but apparently rearranged even at 170° to the 15-ene. In order to effect this elimination under milder conditions, use was made of dimethyl sulphoxide.[12] The hydrocarbon, $C_{17}H_{12}$, isolated in very low yield after the 17-tosylate had been heated at 100° in this solvent for a short time, exhibited an ultraviolet spectrum (see Figure) very similar to that of the 17-methyl-16-ene



Ultraviolet spectra. A, (IXa); B, (IIIa); C, (VIIIa)

(IIIa), but different from that of (VIIIa) by the absence of the 240 mμ peak and by the reversal of the intensities of the maxima at 269 and 273 mμ. Moreover, judging from the ultraviolet spectrum of the product, this compound was isomerised to (VIIIa) when heated at 180°. The same result was also observed when the elimination in dimethyl sulphoxide at 100° was prolonged. It is therefore concluded that the new hydrocarbon is the previously unknown (IXa). The infrared spectra of (VIIIa) and (IXa) differed only in minor details (see Experimental section).

Condensation of the 15-ene (VIIIa) with benzaldehyde in ethanol containing potassium hydroxide gave the 17-benzylidene-15-ene (Xa). On hydrogenation, this compound, which showed strong light absorption at 328 and 383 mμ, absorbed 2 mol. of hydrogen, to yield (XIa), the ultraviolet spectrum of which closely resembled that of the Diels hydrocarbon. Condensation of (VIIIa) with *p*-dimethylaminobenzaldehyde likewise afforded the *p*-dimethylaminobenzylidene compound (Xc), of interest because the corresponding 1-*p*-dimethylaminoindene is claimed [13] to exhibit marked anti-tumour activity. Condensation of (VIIIa) with acetone in the presence of potassium hydroxide did not lead to the isopropylidene derivative (Xb), but this substance was readily secured as a yellow compound ($\lambda_{max.}$ 310 mμ) when the condensation was catalysed by piperidine. A colourless isomer isolated from the potassium hydroxide catalysed reaction had ultraviolet absorption very similar to that of the 17-methyl-16-ene (IIIa) and is consequently assigned the structure (XII). Presumably rotation of the isopropenyl group about the 17-single bond relieves steric compression with the C-12 hydrogen atom and deconjugates the terminal double bond from the ring-system chromophore. The structures proposed for (Xb) and (XII) were confirmed by their n.m.r. spectra; in the methyl and methylene regions the former consisted of two proton singlets at τ 7·52 and 7·69 arising from the two non-equivalent methyl groups, while the latter revealed the presence of one methyl group adjacent to a double bond (3-proton singlet at 8·1) and the C-15 methylene group (2-proton multiplet at 6·18). Hydrogenation of (Xb) readily gave (XIb), but when the reduction was interrupted after the uptake of 2 atoms of hydrogen the expected 17-isopropylidene analogue of (VI) was not obtained. The product instead consisted of a mixture of four compounds, present in comparable amounts. After chromatographic separation these proved to be starting material (Xb), the tetrahydro-derivative (XIb), and two dihydro-compounds. One of the latter was (IXb), from its ultraviolet absorption

TABLE 2

N.m.r. absorptions (τ) of protons attached to the D-ring in cyclopenta[*a*]phenanthrenes

Compound	C-17	C-16	C-15	Other protons
(I)	6·85m(2H)	7·75m(2H)	6·85m(2H)	—
(VIIIa)	6·35m(2H)	(~3·3 *)		—
(IVa) ...	[7·0—8·5(3H) *]		6·78m(2H)	Me, 8·63d(3H)
(IIIa) ...	—	3·55s	6·33t(2H)	Me, 7·75d(3H)
(VI)	—	6·95m(2H)	6·75m(2H)	CH_2 protons 4·44s, 4·87s
(IIa) ...	—	7·3m(2H)	6·7m(2H)	—
(Xb) ...	—	(3·0s, 3·1s)		Me groups 7·52s(3H), 7·69s(3H)
(XII) ...	—	3·25s	6·18d(2H)	Me, 8·1s(3H)

* Unresolved; s = singlet, d = doublet, m = multiplet.

characteristics and melting point.[5] The ultraviolet spectrum of the other was similar to that of (VIIIa), with $\lambda_{max.}$ 269 and a small maximum at 240 mμ, and it must therefore have the Δ^{15}-17-isopropyl structure (VIIIb). The ease of reduction of the tetrasubstituted 16-double bond suggests that this also is a result of the relief of steric strain.

Chemical shifts of the D-ring protons in representatives of the various classes of compound encountered in the present work are summarised in Table 2.

[12] H. R. Nace, *J. Amer. Chem. Soc.*, 1959, **81**, 5428.
[13] C. T. Bahner, H. Kinder, D. Brotherton, J. Spiggle, and L. Gutman, *J. Medicin. Chem.*, 1965, **8**, 390.

EXPERIMENTAL

Experimental conditions are generally as described in Part I (preceding Paper).

Grignard Reactions with 17-Ketones.—To a solution of methylmagnesium iodide [from magnesium turnings (0·8 g.), methyl iodide (1·2 ml.), and dry ether (20 ml.)] was added the ketone (1·0 g.) in dry benzene, and the mixture was heated under reflux for 1 hr. The ether was then removed by distillation, more benzene (20 ml.) was added, and heating was continued for 1 hr. further. The cooled reaction mixture was poured into 10% aqueous ammonium chloride solution (50 ml.) containing 5N-hydrochloric acid (1 ml.), shaken thoroughly with more benzene, separated without delay, and washed with sodium hydrogen carbonate solution. After being dried, the solvent was removed *in vacuo*, and the residue was redissolved in the minimum of dry benzene and chromatographed on a column of alumina (Wöelm, neutral, Brockmann Grade I; 100 g.) using a linear gradient made by continuously mixing benzene (1 l.) with hexane (1 l.). The 17-methyl-16-ene was eluted first, followed by the dimer. The compounds prepared in this way are summarised in Table 3.

Hydrogenation of Δ^{16}*-Compounds.*— The unsaturated compound (500 mg.) in ethanol (100 ml.) was shaken with Adams catalyst (50 mg.) in an atmosphere of hydrogen until the calculated volume of hydrogen had been absorbed. The catalyst was removed by filtration and washed with ethanol, the solution was evaporated to dryness and the residue was recrystallised from ethanol or otherwise as specified in Table 4.

15,16-*Dihydro*-17-*methylenecyclopenta*[a]*phenanthrenes* (VI).—A solution of the methyl Wittig reagent was prepared as follows. A 3·4N-solution of butyl-lithium (12·0 ml.) was added to a suspension of methyltriphenylphosphonium bromide (14·28 g.) in tetrahydrofuran (200 ml.), and the mixture was boiled under nitrogen for 30 min., to give a clear orange solution. After addition of the ketone (IIa) (4·64 g.), the mixture was boiled under reflux in nitrogen for 4 hr. and left overnight at room temperature. Most of the solvent (150 ml.) was removed *in vacuo*, the residue was treated with water (700 ml.), the dark oil was extracted with chloroform, and the solution was dried and evaporated. The residual gum was rapidly chromatographed on alumina (200 g.) with benzene (1 l.); on evaporation, the eluate furnished the 17-*methylene compound* (VI) (2·05 g.) as a cream solid which crystallised from ethanol (350 ml.) as large pale amber leaflets (1·7 g.), m. p. 217—218° (sealed, evacuated capillary tube) (Found: C, 93·65; H, 6·3%; *M*, 240. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%; *M*, 230·3), $\lambda_{max.}$ 215(4·22), 273·5(4·69), 287(4·44), 299(4·34), 307(4·09), 333(3·08), 349(3·28), 367(3·34) mμ, $\nu_{max.}$ ($CHCl_3$) 3·25 (exocyclic CH_2), $\nu_{max.}$ 6·18, 10·62, 11·6, 12·04, 12·42, 13·42, 13·9 μ.

To a hot solution of (VI) (120 mg.) in ethanol (20 ml.) was added 2 drops of conc. hydrochloric acid. After 1 min. the solution was cooled; there separated cream needles (62 mg.) of (IIIa), the infrared spectrum of which was identical with that of this compound prepared by the Grignard reaction from (IIa).

Hydrogenation of (VI) (100 mg.) with Adams catalyst (10 mg.) in ethanol (25 ml.) occurred smoothly. Recrystallisation from ethanol afforded Diels hydrocarbon (IVa) (76 mg.), m. p. 126°.

15,16-*Dihydro*-17-*hydroxycyclopenta*[a]*phenanthrene* (VIIa).—The 17-ketone (IIa) (2·0 g.), tetrahydrofuran (120 ml.), water (8 ml.), and sodium borohydride (2·0 g.) were heated under reflux for 5 hr., the solution was poured into water (1 l.), and the cream precipitate was dried *in vacuo*. The *alcohol* (VIIa) (1·91 g.), m. p. 183—184°, was dried at room temperature over phosphorus pentoxide for

TABLE 3

17-Methyl-15*H*-cyclopenta[*a*]phenanthrenes (III) prepared by Grignard reactions.

					Yield	Found (%) ¶			Required (%)	
(III)	R^1	R^2	R^3	M. p.	(%)	C	H	Formula	C	H
a	H	H	H	209—212° *	60	—	—	$C_{18}H_{14}$	—	—
b	OMe	H	H	204—205 ‡	55	87·5	6·2	$C_{19}H_{16}O$	87·65	6·2
c	H	Me	H	161—162 †	28	93·15	7·05	$C_{19}H_{16}$	93·4	6·6
d	H	H	Me	149—150 †	74	93·6	7·0	$C_{19}H_{16}$	93·4	6·6
e	H	Me	Me	126—126·5 †	32	92·75	6·95	$C_{20}H_{18}$	93·0	7·0
f	H	H	OMe	159—160 †	18 §	87·45	5·85	$C_{19}H_{16}O$	87·65	6·2

* From carbon tetrachloride (Found: *M*, 236. Calc. for $C_{18}H_{14}$: *M*, 230·3); lit.,[5] m. p. 207—209°. The dimer was also isolated, m. p. 203—204° (from benzene) (lit., 192—194°) (Found: *M*, 455), $\lambda_{max.}$ 261·5(4·76), 273(4·80), 283·5(4·92), 300·5(4·44), 324(4·13), mμ, $\nu_{max.}$ 11·6, 12·32, 13·4, 13·88 μ. † From ethanol. ‡ From benzene. § (IIf) prepared according to R. Robinson, *J. Chem. Soc.*, 1938, 1395, was employed. A considerable amount of *dimer*, m. p. 210—212° (from ethanol), was also isolated in this experiment (Found: C, 87·44; H, 6·25%; *M*, 526. $C_{38}H_{32}O_2$ requires C, 87·65; H, 6·2%; *M*, 520·6), $\lambda_{max.}$ 255(4·69), 274(4·87), 289(4·95), 330(4·11), 344(3·92), 361(3·97), 377(3·72) mμ, $\nu_{max.}$ 11·6, 12·0, 12·1, 12·22, 12·54, 13·18, 13·3, 13·9 μ. In a similar experiment, in which chromatography was omitted, the crude product crystallised from ethanol to give (IIIf) (85%), m. p. 155—158°. ¶ Analytical samples were sublimed at 130—150°/10^{-4} mm.

TABLE 4

15,16-Dihydro-17-methylcyclopenta[*a*]phenanthrenes (IV) prepared by hydrogenation.

					Found (%) ‡			Required (%)	
(IV)	R^1	R^2	R^3	M. p.	C	H	Formula	C	H
a	H	H	H	126·5—127·5° *	92·95	6·95	$C_{18}H_{11}$	93·05	6·95
b	OMe	H	H	149—150 §	87·1	6·75	$C_{19}H_{18}O$	87·0	6·9
c	H	Me	H	56—57	92·4	7·45	$C_{19}H_{18}$	92·65	7·35
d	H	H	Me	65	92·65	7·6	$C_{19}H_{18}$	92·65	7·35
e	H	Me	Me	75—77	92·7	8·0	$C_{20}H_{20}$	92·3	7·75
f	H	H	OMe	— †	86·4	6·9	$C_{19}H_{18}$	87·0	6·9

* Diels hydrocarbon, m. p. 125° (Harper, Kon, and Ruzicka, *J. Chem. Soc.*, 1934, 124). † Analysed as a viscous syrup after molecular distillation at 80°/10^{-3} mm. ‡ Analytical samples were sublimed at 70—80°/10^{-4} mm. § Lit., m. p. 146·5—148·5 (Cohen, Cook, and Hewett, *J. Chem. Soc.*, 1935, 445).

2 days (Found: C, 87·0; H, 6·1. $C_{17}H_{14}O$ requires C, 87·15; H, 6·0%), $\lambda_{max.}$ 259(4·77), 280(4·09), 288(3·98), 300(4·12) mμ, $\nu_{max.}$ 3·15 and 9·55 (OH), 11·5, 12·28, 12·92, 13·4, 13·85 μ.

The above alcohol (1·9 g.), toluene-*p*-sulphonyl chloride (1·7 g.), and dry pyridine (25 ml.) were kept at room temperature for 24 hr. The mixture was diluted with water (250 ml.), and the pale brown precipitate was washed with water and dried (2·01 g.), m. p. 167—168°. The *tosyl derivative* (VIIb) formed leaflets (from ethanol), m. p. 178—179° (Found: C, 74·4; H, 5·35. $C_{24}H_{20}O_3S$ requires C, 74·2; H, 5·2%), $\lambda_{max.}$ 220(4·48), 259(4·83), 279(4·23), 288(4·09), 300(4·15) mμ, $\nu_{max.}$ 11·4, 12·24, 12·8, 12·95, 14·0, 14·3, 14·68 μ.

17H-*Cyclopenta*[a]*phenanthrene* (VIIIa).—*From the* 17-*tosylate*. This compound (VIIb) (440 mg.) was boiled under reflux with redistilled collidine (10 ml.) for 30 min. After dilution with chloroform (30 ml.), the solution was washed with N-sulphuric acid (90 ml.), sodium hydrogen carbonate solution, and water. Evaporation of the dried solution left (VIIIa) (202 mg.), m. p. 159—163°; an analytical sample crystallised from ethanol as pale pink needles, m. p. 164—165° (Found: C, 94·55; H, 5·5. Calc. for $C_{17}H_{12}$: C, 94·5; H, 5·6%), $\lambda_{max.}$ 224(4·41), 239(4·24), 269(4·72), 273·5(4·70), 292(4·17), 302·5(4·16), 314·5(4·04) mμ, $\nu_{max.}$ 10·6, 11·0, 11·55, 12·28, 12·8, 13·36, 13·66, 14·4 μ, $\nu_{max.}$(CS_2) 695, 746, 752, 810 cm.$^{-1}$ (measured as a 2% solution on a Perkin-Elmer 237 grating spectrometer).

Hydrogenation of this compound afforded (I), m. p. 134—135° (lit.,[9] 134—135°), $\lambda_{max.}$ 216(4·48), 259(4·77), 280(4·16), 288(4·07), 300(4·17) mμ, $\nu_{max.}$ 10·62, 11·56, 12·3, 12·95, 13·4, 14·08 μ.

From 16,17-*dihydro*-15-*oxocyclopenta*[a]*phenanthrene*. This ketone was prepared by cyclisation of phenanthrene-2-propionic acid according to Bachmann and Kloetzel;[8] it was obtained as pale yellow needles, m. p. 184—186°, $\lambda_{max.}$ 216(4·41), 251·5(4·58), 288(4·06), 319(4·08), 344sh(3·65), 362(3·49) mμ, $\nu_{max.}$ 5·9 (conjugated C=O) 10·32, 10·4, 11·4, 11·76, 11·9, 12·26, 12·92, 13·2, 13·94 μ.

Reduction of this ketone (5·0 g.) with sodium borohydride as described above gave the 15-alcohol (4·85 g.), m. p. 164—165° (lit.,[14] 166—167°). This alcohol was converted into its tosylate, and the crude material was heated with collidine, as described above. Chromatography of the elimination product on alumina with hexane–benzene (1 : 1) then afforded (VIIIa) as needles (1·08 g.), m. p. 161 and 161—164° when mixed with the analytical specimen derived from the 17-ketone. The ultraviolet and infrared spectra of the two specimens were superimposable.

15H-*Cyclopenta*[a]*phenanthrene* (IXa).—The 17-tosylate (VIIb) (5·0 g.) was kept at 100° with dimethyl sulphoxide (25 ml.) for 30 min. The temperature of the bath was then lowered to 50° and the solution was evaporated to dryness on an oil pump to give a solid which was triturated with hexane–dichloromethane (9 : 1; 100 ml.). Chromatography of the extract on silica gel (100 g.) using this solvent mixture as eluant yielded crystals (149 mg.), $\lambda_{max.}$ 273·5 mμ, no maximum at 240 mμ. This material was crystallised rapidly from warm ethanol, to give the *product* (IXa) (63 mg.), m. p. 165—167° (with change of crystal form at 150°) (Found: C, 94·35; H, 6·0%), $\lambda_{max.}$ 220(4·45), 269 (4·795), 273(4·81), 292(4·23), 302(4·17), 314(3·96) mμ, $\nu_{max.}$(CS_2) 698, 748, 814 cm.$^{-1}$ (measured as a 2% solution on a Perkin-Elmer 237 grating spectrometer). When the reaction was allowed to proceed at 100° for 6 hr., the material recovered exhibited $\lambda_{max.}$ 239 and 269 mμ. The same result was observed when a small sample of (IXa) was heated at 180° in a sealed, evacuated glas tube for 30 min.

17-*Isopropenyl*-15H-*cyclopenta*[a]*phenanthrene* (XII).—The compound (VIIIa) (100 mg.) was dissolved in acetone (2·0 ml.) and treated with a solution (0·001 ml.) containing potassium hydroxide (250 mg.) in methanol (1·0 ml.). An orange colour rapidly developed, and within 2 hr. crystals filled the liquid. The crystals (40 mg.), m. p. 250—255°), were recrystallised from benzene (2 ml.), to furnish the *isopropenyl compound* (XII) as needles, m. p. 255° (Found: C, 93·95; H, 6·35. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%), $\lambda_{max.}$ 223(4·40), 271(4·74), 276(4·75), 295(4·30), 316(3·40) mμ. $\nu_{max.}$ 10·2, 10·9, 12·08, 12·38, 12·86, 13·48, 14·6 μ.

17-*Isopropylidenecyclopenta*[a]*phenanthrene* (Xb).— The 15-olefin (VIIIa) (250 mg.) was dissolved in acetone (6·5 ml.) containing piperidine (100 mg.) and left at room temperature in a sealed flask for 2 days. The solution became yellow and yellow crystals separated. The solvent was evaporated *in vacuo* and the residue was recrystallised from n-butanol. The *isopropylidene compound* (Xb) formed bright yellow leaflets (251 mg.), m. p. 188—189° (Found: C, 93·6; H, 6·4%), $\lambda_{max.}$ 214(4·44), 228(4·50), 270(4·63), 302(4·67), 310(4·77), 345—349sh(3·61), 364—369sh(3·50) mμ, $\nu_{max.}$ 6·1 (conjugated C=C) 11·66, 12·0, 12·14, 12·5, 13·2 μ.

The isopropylidene compound (23·8 mg.) in ethyl acetate (5 ml.) was hydrogenated using 5% palladium–charcoal (21 mg.). Uptake of 2 mol. of hydrogen was complete within 15 min. Evaporation of the colourless, filtered solution, and recrystallisation of the residue from methanol (1 ml.), gave needles (15 mg.), m. p. 97—98° (lit.,[15] 97—98°) of (XIb) (Found: C, 92·6; H, 8·0. Calc. for $C_{20}H_{20}$: C, 92·25; H, 7·75%), $\lambda_{max.}$ 216(4·51), 259(4·79), 281(4·17), 288(3·86), 300(4·14) mμ, $\nu_{max.}$ 11·54, 12·38, 13·0, 13·34 μ.

The isopropylidene compound (25·1 g.) was hydrogenated as above with 2 mg. of catalyst, and shaking was interrupted when 1 mol. of hydrogen had been absorbed (17 min.). The filtered solution was evaporated, and the pale yellow residue was chromatographed on a column of silica gel (29 × 1 cm.; 10 g.) with hexane, collecting 10-ml. fractions. Fractions 10—16 gave crystals (4·2 mg.), m. p. 85—93°, of the saturated compound (XIb). Fractions 17—23 were combined, and yielded crystals (7·1 mg.), m. p. 105—107°, raised to 106—107° after one crystallisation from methanol, of the *isopropyl compound* (VIIIb) (Found: 93·2; H, 6·9. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%), $\lambda_{max.}$ 221(4·66), 240(4·33), 269(4·65), 274(4·60), 292·5(4·07), 303(4·075), 317(3·95) mμ, $\nu_{max.}$ 10·30, 10·52, 10·76, 10·9, 11·5, 12·3, 13·0, 13·26, 13·65, 14·0 μ. Further elution with hexane (fractions 24—40) gave crystals (6·0 mg.), m. p. 135—142°, raised to 150—153° (lit.,[5] 154—155°) by recrystallisation from methanol, of (IXb), $\lambda_{max.}$ 224(4·31), 271(4·70), 275(4·71), 316(4·02) mμ, $\nu_{max.}$ 10·26, 10·9, 11·5, 12·22, 12·9, 13·34, 13·66 μ. Finally, elution of the yellow band with benzene–hexane (1 : 1) gave yellow crystals (4·0 mg.), m. p. 172—176°, of the starting material (Xb).

17-*Benzylidenecyclopenta*[a]*phenanthrene* (Xa).—To a solution of the 15-olefin (VIIIa) (210 mg.) in ethanol (15 ml.) containing benzaldehyde (120 mg.) was added a saturated

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

[15] B. Riegel, M. H. Gold, and M. A. Kubico, *J. Amer. Chem. Soc.*, 1943, **65**, 1772.

solution (0·5 ml.) of potassium hydroxide in ethanol. An orange crystalline solid rapidly separated; after 30 min. on a steam-bath, the solution was cooled and the solid was dried (231 mg.), m. p. 257—259°. The *benzylidene compound* (Xa) formed orange, feathery needles (from toluene,) m. p. 262—263° (Found: C, 94·9; H, 5·55. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%), $\lambda_{max.}$ 249(4·52), 328(4·65), and 384(4·07) mμ, $\nu_{max.}$ 12·05, 12·47, 13·12, 13·38, and 14·44 μ.

Hydrogenation of this compound (100 mg.) in ethyl acetate (20 ml.) over 5% palladium–charcoal (100 mg.) stopped with the uptake of 2 mol. of hydrogen. After filtration, the colourless solution was evaporated, and the residue was recrystallised from ethanol, to furnish the *benzyl compound* (XIa) (73 mg.), m. p. 156—157° (Found: C, 93·4; H, 6·7. $C_{24}H_{20}$ requires C, 93·45; H, 6·55%), $\lambda_{max.}$ 216(4·46), 260(4·81), 281(4·20), 289(4·08), 301(4·14), 320(2·77), 336(2·98), 352(3·00) mμ, $\nu_{max.}$ 12·1, 12·36, 12·96, 13·3, 13·48, 14·28 μ.

17-p-*Dimethylaminobenzylidenecyclopenta*[a]*phenanthrene* (Xc).—Condensation of (VIIIa) (170 mg.) with *p*-dimethylaminobenzaldehyde (117 mg.) in the presence of potassium hydroxide as described above gave the *compound* (Xc) (165 mg.) as a bright yellow microcrystalline solid, m. p. 248—250° (Found: C, 90·05; H, 6·25. $C_{26}H_{21}N$ requires C, 89·9; H, 6·1%), $\lambda_{max.}$ 371(4·18), 434(4·58) mμ, $\nu_{max.}$ 12·15, 12·32, 12·58, 13·24, 13·5 μ.

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