Potentially Carcinogenic Cyclopenta[*a*]phenanthrenes. Part VIII.[1] Bromination of 17-Ketones

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Bromination of 15,16-dihydrocyclopenta[*a*]phenanthren-17-one and its 11-methyl homologue gave the 15-bromo- and 15,15-dibromo-derivatives, even under conditions favouring aromatic bromination. *N*-Bromosuccinimide introduced bromine adjacent to the carbonyl group. Reductive tritiation of the 15-bromo-ketone gave the [15-^{3}H]-derivative, but nucleophilic displacement of the bromine atom with sodium acetate in acetic acid led unexpectedly to the 16-acetoxy-17-ketone. Acid-catalysed hydration of the 15(16)-en-17-one, readily prepared by dehydrobromination of the 16-bromo-17-ketone with triethylamine, yielded the 15-hydroxyketone. The acetate of the latter was the major product from attempted bromination of the 17-ketone in the presence of thallium triacetate.

BROMINATION of phenanthrene under a variety of conditions leads to substitution at the 9- and 10-positions.[2] We considered that, by analogy, bromination of 15,16-dihydrocyclopenta[*a*]phenanthren-17-one (Ia) would yield 6- or 7-bromo derivatives, especially since these positions (as in phenanthrene) are attacked by reagents such as osmium tetroxide and chromic acid.[3] It was hoped that the expected 6- and 7-bromo derivatives, by reductive debromination in tritium gas, would furnish these ketones labelled specifically with tritium at very high specific activity,[4] making them available for biological experiments in connection with the high carcinogenic activity of the 11-methyl-17-ketone (Ib).[5] In the event this aim was not achieved, and the results described in this paper emphasize the substantial reactivity of the five-membered ring in compounds of this series.

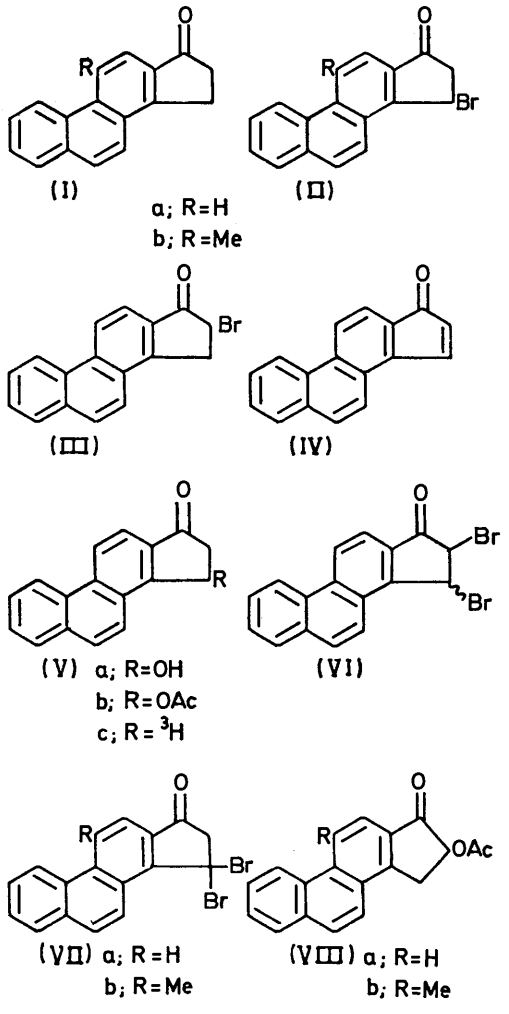
Treatment of the unsubstituted ketone (Ia) with 1 equiv. of bromine in chloroform or acetic acid gave a mono- and a dibromo-derivative. The former proved to be the 15-bromo-17-ketone (IIa) since its n.m.r. spectrum exhibited signals of an ABX system, corresponding to two non-equivalent methylene protons coupled to a strongly deshielded methine proton (see Table). Moreover, reductive debromination in a mixture of tritium and hydrogen gas gave the [15-^{3}H]-17-ketone (Vc) which retained its label both on treatment with alkali and on oxidation to the 6,7-quinone,[3] proving that the tritium was not at C-6, -7, or -16.

Bromination of the ketone (Ia) with *N*-bromosuccinimide gave a different monobromo-derivative in high yield. This bromo-ketone also exhibited an ABX system in its n.m.r. spectrum and is thus the 16-bromo-17-ketone (III). Reduction of this compound with sodium borohydride gave the *cis*-bromohydrin, since the product was stable to alkali. Dehydrobromination of (III) occurred readily, being essentially complete within 10 min at room temperature on treatment with triethylamine in tetrahydrofuran, or with 2 equiv. of aqueous sodium hydroxide in dioxan. Cyclopenta[*a*]phenanthren-17-one (IV) formed bright orange crystals with characteristic u.v. absorption, but purification was complicated by the ease with which it gave rise to insoluble material on storage or attempted recrystallisation. In this respect it resembles the analogous system indenone.[6] Treatment of the 16-bromide (III) with sodium acetate in acetic acid also gave insoluble, intract-

[1] Part VII, M. M. Coombs and M. Hall, *J.C.S. Perkin I*, 1973, 1255.
[2] C. A. Dornfeld, J. E. Callan, and G. H. Coleman, *Org. Synth.*, Coll. Vol. III, 1955, 134.
[3] M. M. Coombs, *J. Chem. Soc.* (*C*), 1969, 2484.
[4] M. M. Coombs and H. R. Roderick, *Steroids*, 1968, 925.
[5] M. M. Coombs and C. J. Croft, *Progr. Experimental Tumor Research*, 1969, **11**, 69.
[6] C. S. Marvel and C. W. Hinman, *J. Amer. Chem. Soc.*, 1954, **76**, 5435.

able material, presumably through prior elimination to the enone (IV).

Similar attempted displacement of bromine from the 15-bromo-17-ketone (IIa) led smoothly, not to the



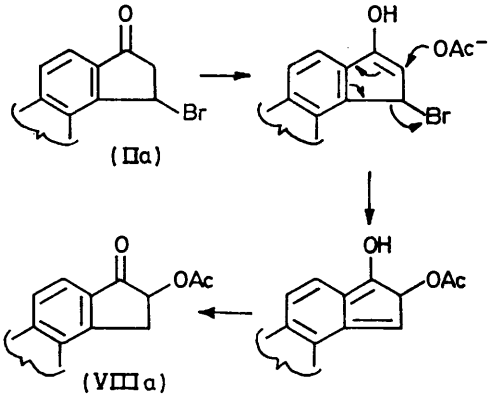
expected 15-acetoxy-compound, but to the 16-acetoxy-17-ketone (VIIIa) identical with the compound previously obtained by oxidation of the parent ketone (Ia) with lead tetra-acetate.[3] Formation of this compound probably occurs by nucleophilic attack by an acetate anion at C-16 in the enol with concomitant expulsion of bromide from C-15 (Scheme 1), since the 15-bromide (IIa) showed no evidence of rearrangement to the isomeric 16-bromide (III) under the reaction conditions employed, but without potassium acetate. The 15-acetoxy-17-ketone (Vb) was prepared, again by analogy with indenone,[7] by acid-catalysed hydration of the 15(16)-double bond in the enone (IV) using aqueous sulphuric acid in tetrahydrofuran at room temperature, followed by acetylation. The structure (Vb), rather than the isomeric 17-acetoxy-15-ketone structure, was assigned to this compound on the basis of its u.v. absorption characteristics which are very similar to those of the 17-ketones (Ia and b) and quite different from those of the 15-ketone of this series.[3] A substantial quantity of insoluble pink solid precipitated out during this reaction, and a minor reaction product was the ketone (Ia). This compound was also formed when the elimination of the 16-bromide with triethylamine was carried out in boiling benzene. It would therefore appear that (Ia) is produced from the enone (IV) by abstraction of

N.m.r. chemical shifts (τ) and coupling constants (Hz) of ring-D protons in bromo- and acetoxy-17-ketones measured in deuteriochloroform

	C(16)-Protons		C(15)-Protons	
Compound	H_A	H_B	H_C	H_D
(IIa)	6·32q J_{AB} 18, J_{AC} 3	5·81q J_{AB} 18, J_{BC} 7	5·17q J_{AC} 3, J_{BC} 7	
(IIb)	6·28q J_{AB} 18, J_{AC} 3	5·77q J_{AB} 18, J_{BC} 7	5·15q J_{AC} 3, J_{BC} 7	
(VIIa)	← 5·31s →			
(VIIb)	← 5·34s →			
(VI)	3·90s		4·95s	
(III)	4·04q J_{AD} 6, J_{AC} 2		6·80q J_{CD} 18, J_{AC} 2	6·52q J_{CD} 18, J_{AD} 6
(Vb)	7·29q J_{AB} 18, J_{AC} 2	6·65q J_{AB} 18, J_{BC} 6	3·17q J_{AC} 2, J_{BC} 6	
(VIIIa)	4·37q J_{AD} 7·5, J_{AC} 4		6·75q J_{CD} 17, J_{AC} 4	5·87q J_{CD} 17, J_{AD} 7·5
(VIIIb)	4·52q J_{AD} 8, J_{AC} 4		6·83q J_{CD} 18, J_{AC} 4	6·01q J_{CD} 18, J_{AD} 8

hydrogen, presumably from the solvent or a second molecule of the phenanthrene.

Bromination of the 15-bromo-17-ketone (IIa) with *N*-bromosuccinimide led to a dibromo-compound which was different from that obtained by bromination of (Ia) with molecular bromine. The n.m.r. spectrum of the former showed two one-proton singlets arising from two chemically and magnetically different protons, and was therefore the 15,16-dibromide (VI). The product from



SCHEME 1

the reaction with bromine was assigned as the 15,15-dibromide (VIIa) because it had a two-proton singlet at τ 5·31 in its n.m.r. spectrum.

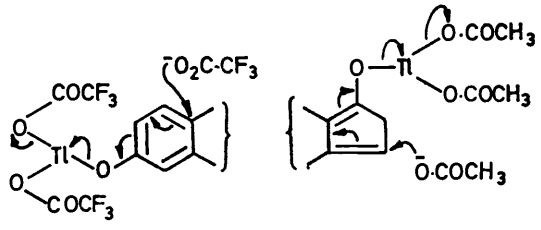
Bromination of the carcinogenic ketone (Ib) with

[7] P. H. Lacey and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1971, 41.

bromine in chloroform also gave mono- and di-bromo-derivatives, the structures of which were readily established as the 15-bromo- and 15,15-dibromo-17-ketones, (IIb) and (VIIb), by n.m.r. spectroscopy.

In an attempt to direct bromination of (Ia) to the aromatic rings, the reaction with bromine in acetic acid was carried out with complete exclusion of light, but the same mixture of 15-bromo- and 15,15-dibromo-derivatives was isolated. Bromination with bromine in the presence of silver nitrate and acid,[8] a method reported to favour electrophilic bromination owing to the liberation of Br^+ cations, also gave the same mixture of bromoketones together with a variety of other products which was not investigated.

Recently thallium triacetate has been recommended[9] as a good catalyst for aromatic bromination. Treatment of the ketone (Ia) with one equivalent of bromine in carbon tetrachloride in the presence of thallium triacetate gave small amounts of the usual bromoketones, together with a compound $C_{19}H_{14}O_3$ as major product. The latter was characterised as the 15-acetoxy-17-ketone (Vb), identical with the product of acetylation of the 15-alcohol, described above. It was not formed when either the ketone (Ia) or the 15-bromoketone (IIa) was treated with thallium triacetate in carbon tetrachloride, and the best yield of (Vb) was secured when the bromine was added in one lot to the mixture of (Ia) and thallium triacetate. It therefore seems probable that a bromo-derivative of Tl^{III} is involved, possibly allowing nucleophilic attack of acetate at C-15 by a mechanism involving an enolic thallic ester (Scheme 2), similar to that recently proposed to account for the formation of 10β-trifluoroacetoxy-19-norandrosta-1,4-diene-3,17-dione by the action of thallium tris(trifluoroacetate) on oestrone.[10]



SCHEME 2

EXPERIMENTAL

Materials and methods were generally as described in previous parts of this series.

15-Bromo- and 15,15-Dibromo-15,16-dihydrocyclopenta[a]*phenanthren-17-ones*, (IIa) *and* (VIIa).—A solution of bromine (2·09 g) in dry chloroform (50 ml) was added dropwise with stirring during 2 h to a solution of 15,16-dihydrocyclopenta[*a*]phenanthren-17-one (3·00 g) in chloroform (200 ml), and after stirring at room temp. for 20 h, the solvent was removed under reduced pressure to leave a brown solid (3·58 g). Chromatography on Wöelm Grade II alumina using toluene gave two substances, from first fractions an orange solid (0·597 g) and from later fractions a cream solid (1·603 g). Crystallisation of the latter from n-butanol gave *15-bromo-15,16-dihydrocyclopenta*[a]*phenanthren-17-one* (IIa) (1·455 g), m.p. 196—197° (Found: C, 65·35; H, 3·35; Br, 25·4. $C_{17}H_{11}BrO$ requires C, 65·6; H, 3·55; Br, 25·7%), $\lambda_{max.}$ (EtOH) 267·5 (log ε 4·78), 286·5 (4·41), 298·5 (4·36), 310 (4·13), 354 (3·32), and 372 nm (3·31), $\nu_{max.}$ (Nujol) 1711 (C=O), 820, and 757 cm^{-1}. Several crystallisations of the orange solid from n-butanol gave *15,15-dibromo-15,16-dihydrocyclopenta*[a]*phenanthren-17-one* (VIIa) (0·428 g), m.p. 213—213·5° (Found: C, 52·25; H, 2·25; Br, 41·2. $C_{17}H_{10}Br_2O$ requires C, 52·35; H, 2·3; Br, 41·0%), $\lambda_{max.}$ (EtOH) 279 (log ε 4·70), 298 (4·24), 314·5 (4·18), 360 (3·30), and 377 nm (3·27), $\nu_{max.}$ (Nujol) 1710 (C=O), 816, and 716 cm^{-1}.

Use of glacial acetic acid in place of chloroform in this bromination gave the same two products in a similar ratio, even when light was carefully excluded.

Bromination in the presence of silver ions was carried out as follows. To a stirred solution of the ketone (Ia) (116 mg) in a mixture of glacial acetic acid (30 ml) and water (10 ml) containing silver nitrate (85 mg) was added a solution of bromine (80 mg) in glacial acetic acid (0·57 ml) dropwise with exclusion of light. After 5 h water was added and the mixture was extracted with dichloromethane. T.l.c. disclosed at least five products, prominent among which was the 15-bromoketone (IIa).

Bromination of the 15-Bromoketone (IIa) *with N-Bromosuccinimide*.—The 15-bromoketone (IIa) (200 mg) in carbon tetrachloride (10 ml) was boiled with *N*-bromosuccinimide (114 mg) for 1 h adjacent to a 150 W lamp. After dilution with more carbon tetrachloride, the cooled solution was washed with water, dried, and evaporated to yield an orange solid (235 mg). Recrystallisation from carbon tetrachloride gave *15,16-dibromo-15,16-dihydrocyclopenta*[a]*phenanthren-17-one* (VI), m.p. 179—180°; the mixed m.p. with the 15,15-dibromoketone (m.p. 213—213·5°) was 165—175° (Found: C, 52·65; H, 2·3; Br, 41·35%), $\lambda_{max.}$ (EtOH) 283 (log ε 4·60), 311·5 (4·33), 361 (3·19), and 380 nm, (3·18), $\nu_{max.}$ (Nujol) 1717 (C=O), 831, and 760 cm^{-1}.

Bromination of 15,16-Dihydro-11-methylcyclopenta[a]*phenanthren-17-one*.—This ketone (Ib) (436 mg) in chloroform (15 ml) was treated with a solution of bromine (279 mg) in chloroform (20 ml) as already described. After 20 h the solvent was removed to leave a brown solid (603 mg), chromatography of which on silica gel (100 g) with toluene–dichloromethane (3 : 1) gave two substances. From the first fractions was obtained an orange solid (134 mg) and from later fractions a yellow solid (395 mg). Several recrystallisations of the former from n-butanol gave orange crystals (38·5 mg) of *15,15-dibromo-15,16-dihydro-11-methylcyclopenta*[a]*phenanthren-17-one* (VIIb), m.p. 206—207° (Found: C, 53·6; H, 2·8; Br, 39·1. $C_{18}H_{12}Br_2O$ requires C, 53·5; H, 3·0; Br, 39·55%), $\lambda_{max.}$ (EtOH) 267·5 (log ε 4·68), 302·5 (4·32), 315sh (4·12), 369 (3·29), and 384 nm (3·31), $\nu_{max.}$ (Nujol) 1712 (C=O), 823, 744, 718, and 708 cm^{-1}. Recrystallisation of the yellow solid from the same solvent furnished yellow needles (247 mg) of *15-bromo-15,16-dihydro-11-methylcyclopenta*[a]*phenanthren-17-one* (IIb), m.p. 211·5—212° (Found: C, 66·8; H, 4·0; Br, 24·45. $C_{18}H_{13}BrO$ requires C, 66·5; H, 4·05; Br, 24·55%), $\lambda_{max.}$ (EtOH) 267·5 (log ε 4·68), 290 (4·37), 303 (4·29), 363 (3·31), and

[8] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 1950, 573.

[9] A. McKillop, D. Bromley, and E. C. Taylor, *J. Org. Chem.*, 1972, **37**, 88.

[10] M. M. Coombs and M. B. Jones, *Chem. and Ind.*, 1972, 169.

381 nm (3·35), $\nu_{max.}$ (Nujol) 1700 (C=O), 820, 759, 722, and 700 cm^{-1}.

16-*Bromo*-15,16-*dihydrocyclopenta*[a]*phenanthren*-17-*one* (III).—The ketone (Ia) (2·320 g, 10 mmol) and *N*-bromosuccinimide (1·850 g, 10·5 mmol) in carbon tetrachloride (100 ml) were boiled under reflux with illumination from an adjacent 150 W lamp. After 2 h the yellow solution containing precipitated succinimide was cooled, diluted with carbon tetrachloride, extracted with water, dried, and evaporated to give a pale brown crystalline solid. Recrystallisation from benzene gave the 16-*bromo*-17-*ketone* (III) as golden laths (1·950 g), m.p. 175° (decomp.) (Found: C, 65·3; H, 3·4; Br, 26·3%), $\lambda_{max.}$ (EtOH) 230·5 (log ε 4·28), 273 (4·73), 300·5sh (4·27), 335sh (3·00), 354 (3·13), and 371 nm (3·13), $\nu_{max.}$ (Nujol) 1700 (C=O), 816, and 756 cm^{-1}.

The bromoketone (III) (100 mg) was treated with sodium borohydride (15 mg) in a mixture of dioxan (2·0 ml) and ethanol (1·0 ml) for 40 h at room temp. Addition of water precipitated the *cis*-bromohydrin as a white solid (48 mg), $\lambda_{max.}$ (EtOH) 256·5, 278, and 299 nm, $\nu_{max.}$ (Nujol) 3320 cm^{-1} (OH). This material was recovered unchanged after it had been left for 20 h dissolved in ethanol containing 1 equiv. of potassium hydroxide.

Dehydrobromination of the 16-*Bromo*-17-*ketone* (III).—*With aqueous potassium hydroxide in dioxan.* The bromoketone (III) (30 mg), dissolved in dioxan (1 ml), was treated with 10% (w/v) aqueous potassium hydroxide (0·1 ml). The solution became orange, and after 15 min was warmed gently. Addition of water precipitated an orange solid which was collected, washed with water, and dried *in vacuo*. This material (20 mg) was warmed with hexane (10 ml), and the solution was filtered. On concentration and cooling bright orange prisms of *cyclopenta*[a]*phenanthren*-17-*one* (IV) separated, m.p. 202—208° (Found: C, 89·3; H, 4·2; M^+ 230·0735. $C_{17}H_{10}O$ requires C, 88·7; H, 4·4%; *M*, 230·0732), $\nu_{max.}$ (Nujol) 1710 (conjugated C=O), 810, 770, and 756 cm^{-1}, $\lambda_{max.}$ (EtOH) 253, 286, 298, and 310 nm, rapidly giving the chromophore $\lambda_{max.}$ 242, 270, and 290 nm characteristic of the 17*H*-15(16)-ene system,[11] on addition of sodium borohydride. The crystals of (IV) became insoluble in hexane on storage at room temp. or on attempted recrystallisation.

With triethylamine in tetrahydrofuran. The bromoketone (III) (100 mg) was dissolved in dry tetrahydrofuran (5 ml) and treated with triethylamine (0·1 ml); the solution became orange and crystalline solid separated. The u.v. spectra of aliquot portions of the solution, removed at intervals and diluted with ethanol, indicated that after 10 min, conversion into the enone (IV) was complete. The reaction mixture was diluted with benzene, washed with ice-cold water, filtered, and dried. Evaporation below 40° under reduced pressure gave an orange crystalline solid, the i.r. spectrum of which was identical with that of the sample of (IV) already described.

With triethylamine in boiling benzene. The bromoketone (III) (575 mg) was heated under reflux with a mixture of triethylamine (10 ml) and dry benzene (10 ml) for 30 min, giving a deep red solution and a brick-red solid. After addition of further benzene the solid was filtered off, and the solution was washed with water and dried. Removal of the solvent left a deep orange syrup (264 mg) which crystallised, m.p. 175—190°, $\lambda_{max.}$ (EtOH) 250infl., 265, 284, 297, and 310 nm. Attempts to purify this material by recrystallisation or chromatography led to further quantities of insoluble red solid, and the only pure compound isolated was a small amount of the ketone (Ia), m.p. 198—199°, u.v. spectrum identical with that of authentic (Ia).

With potassium acetate in acetic acid. The bromoketone (III) (1·0 g) in acetic acid (20 ml) was heated on a steam-bath with potassium acetate (2·0 g) for 6 min to give a deep red solution filled with flocculent solid. The mixture was diluted with ethyl acetate, insoluble material (283 mg) was collected, and the solution was washed with water, and dried. The orange oil obtained on evaporation no longer dissolved completely in ethyl acetate. Filtration of the solution and re-evaporation left an orange gum, $\lambda_{max.}$ (EtOH) 269, 297, and 310 nm, which on storage in the refrigerator became partly insoluble in this solvent.

Reaction of the 15-*Bromo*-17-*ketone* (IIa) *with Potassium Acetate in Acetic Acid.*—The 15-bromoketone (IIa) (200 mg), acetic acid (20 ml), and potassium acetate (1·0 g) were heated under reflux for 20 h. The acetic acid was removed under reduced pressure, the residue was shaken with saturated sodium chloride solution and ethyl acetate, and the latter was washed with aqueous sodium hydrogen carbonate, and dried. Evaporation left a buff solid (183 mg), recrystallisation of which from benzene gave 16-acetoxy-15,16-dihydrocyclopenta[*a*]phenanthren-17-one (VIIIa), m.p. 177·5—178°, mixed m.p. 178—179° with an authentic sample.[3] The i.r. and u.v. spectra of this material were also identical with those of the authentic material. The 15-bromoketone (IIa), m.p. and mixed m.p. 192—193°, was unchanged when a sample (20 mg) was boiled under reflux with glacial acetic acid (2·0 ml) for 20 h and worked up as described above. The u.v. spectrum of the recovered material was identical with that of (IIa).

[15-^{3}H]-15,16-*Dihydrocyclopenta*[a]*phenanthren*-17-*one* (Vc).—The 15-bromo-17-ketone (IIa) (3·1 mg) and 5% Pd–$CaCO_3$ (3·5 mg) in ethanol (1·5 ml) were stirred together in an atmosphere of hydrogen containing *ca.* 0·5% v/v of tritium gas. After 30 min, when absorption of gas had ceased, the mixture was added to water (10 ml) and extracted with benzene (2 × 5 ml). The benzene extract was washed with 5% (w/v) aqueous sodium hydroxide (5 × 5 ml), then twice with water, and finally diluted to 100·0 ml with benzene. This solution contained 840 μCi of tritium and on t.l.c. ran as a single spot with R_F values, u.v. absorption, and fluorescence under u.v. light indistinguishable from those of authentic (Ia). Further extraction of the benzene solution with aqueous alkali removed no radioactivity.

Radioinactive ketone (Ia) was added to a portion of the benzene solution to give a sample of (Vc) with a specific activity of 78·6 μCi $mmol^{-1}$. This ketone (92 mg) was stirred with a solution of chromium trioxide (150 mg) in glacial acetic acid (10 ml). After 24 h the yellow precipitate of the 6,7-quinone[3] was collected, washed with water, and dried. Recrystallisation from boiling toluene gave golden yellow leaflets, specific activity 72·3 μCi $mmol^{-1}$.

15-*Acetoxy*-15,16-*dihydrocyclopenta*[a]*phenanthren*-17-*one* (Vb).—The 16-bromoketone (III) (620 mg) in tetrahydrofuran (50 ml) was stirred with triethylamine for 15 min. 5N-H_2SO_4 (50 ml) was added and the deep orange solution was stirred at room temp. for 24 h, when the reaction mixture consisted of a pink solid suspended in an orange solution. Water (200 ml) was added and the mixture was shaken with an equal volume of ethyl acetate. The solid was filtered off, washed with water and ethyl acetate, and dried (216 mg). The ethyl acetate layer was separated,

[11] M. M. Coombs, *J. Chem. Soc.* (*C*), 1966, 963.

washed with water, dried, and evaporated to yield a partly solid orange gum (187 mg). This material was acetylated with acetic anhydride (2 ml) in dry pyridine (2 ml) overnight. After addition of water, the mixture was extracted with dichloromethane and the extract was washed with 2N-H_2SO_4, then with water until neutral, and dried. Evaporation gave a dark brown gum (188 mg) which was chromatographed on silica gel (60 g). Fractions eluted with dichloromethane containing 2% v/v ethyl acetate and shown by t.l.c. to contain the 15-acetate were combined (55 mg). Two recrystallisations of this solid from hot n-butanol gave the 15-acetoxy-17-ketone (Vb) as cream needles, m.p. 197—198°, and 197—199° when mixed with a sample of this compound obtained by treatment of (Ia) with thallium triacetate and bromine (see below).

Treatment of the Ketone (Ia) *with Thallium Triacetate and Bromine.*—The ketone (Ia) (464 mg, 2 mmol) and thallium triacetate (763 mg, 2 mmol) were stirred together in carbon tetrachloride (100 ml), a solution of bromine (320 mg, 2 mmol) in carbon tetrachloride was added, and the mixture was stirred at room temp. for 22 h. The solid was collected and washed with the same solvent. The solution and washings were shaken with aqueous sodium hydrogen carbonate solution and with water, and dried; evaporation of the solvent left a yellow gum (297 mg).

This gum and material from a similar experiment (total, 615 mg) were chromatographed on a column of silica gel (60 g), eluting with dichloromethane. The first fractions contained a mixture (62 mg) of the bromoketones (IIa) and (VIIa), identified by their R_F values and u.v. light absorption characteristics. Subsequent fractions consisted of the starting material (Ia) and the product (Vb) (together, 236 mg) in the approximate ratio 1 : 2. Rechromatography of this material gave the 15-*acetoxy*-17-*ketone* (Vb) which after repeated recrystallisation from n-butanol, then ethanol, had m.p. 198·5—199° (Found: C, 78·9; H, 4·6; M^+, 290·0949. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·85%; M 290·0943), $\nu_{max.}$ (Nujol) 1740 (acetate), 1710 (ketone), 1022, 855, 820, and 757 cm^{-1}, $\lambda_{max.}$ (EtOH) 269 (log ε 4·76), 297 (4·26), 330sh (3·10), 349 (3·09), 366 (3·07) nm.

When this procedure was repeated, but with omission of bromine, or when the 15-bromoketone (IIa) (10 mg) and thallium triacetate (12·5 mg) were stirred together in carbon tetrachloride (2 ml) for 22 h, the starting materials appeared unchanged and no new compounds had appeared, as judged by t.l.c.

We thank the Imperial Cancer Research Fund for a Bursary (to C. W. V.). We are indebted to Dr. R. B. Boar for helpful criticism of the manuscript, and to D. W. Thomas for the microanalyses.

[3/994 *Received*, 16*th May*, 1973]