308. *The Birch Reduction of Some Substituted Octahydro-2-hydroxy-12-methylphenanthrenes.*

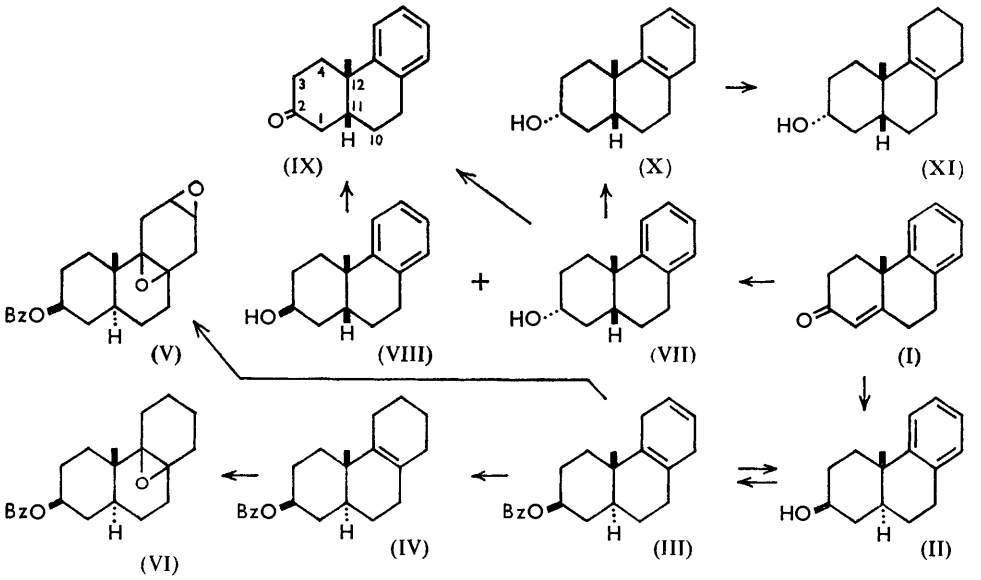
By F. H. Howell and D. A. H. Taylor.

Reduction of derivatives of 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-2-hydroxy-12-methylphenanthrene with sodium and methanol in liquid ammonia proved disappointing. The expected products of addition of two hydrogen atoms were obtained, but the parent compound was extremely difficult to reduce, while the more reactive 6- and 7-methoxylated derivatives gave small yields, as the methoxy-group was also lost.

Reduction of *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-2β-hydroxy-12-methylphenanthrene * (II) or, more conveniently, the unsaturated ketone 2 : 3 : 4 : 9 : 10 : 12-hexahydro-12-methyl-2-oxophenanthrene (I) with 100 equivalents of sodium in methanol and

* The stereochemical nomenclature used in this paper is as follows: *trans* and *cis* refer to the 11 : 12-ring-junction positions; α and β are used in the steroid sense with the 12-methyl group arbitrarily considered as β. All the compounds recorded are optically inactive, and formulæ and names should be held to include the mirror images.

liquid ammonia gave 72% of *trans*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-decahydro-2β-hydroxy-12-methylphenanthrene, isolated as its crystalline benzoate (III). A smaller amount of sodium left unchanged starting material. The use of lithium in place of sodium was unsatisfactory as an insoluble lithium salt separated.



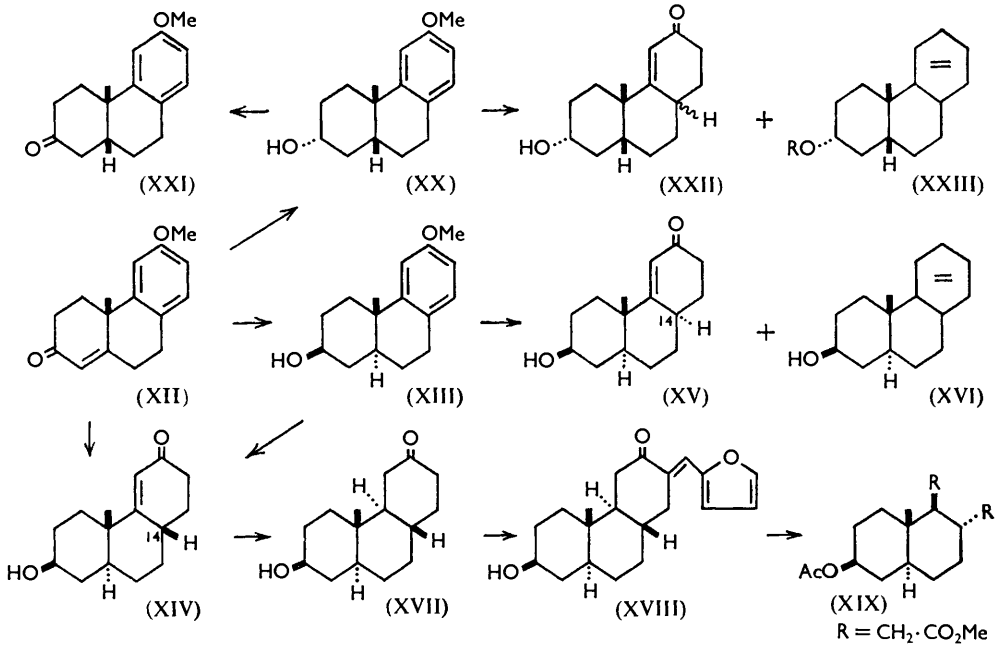
Addition of two hydrogen atoms at the unsubstituted *para*-position of an aromatic ring as in (III) is usual in a Birch reduction, and the structure is supported by the reactions of the compound, and by the fact that the free alcohol showed no selective ultraviolet absorption. Permanganate oxidation of the benzoate (III) gave the benzoate of the original alcohol (II), and performic acid gave a diepoxide (V). On hydrogenation over palladised calcium carbonate, compound (III) took up one mol. of hydrogen, giving *trans*-2β-benzoyloxy-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-dodecahydro-12-methylphenanthrene (IV). This was unaffected by permanganate, but gave an epoxide (VI) with performic acid. On hydrogenation of the benzoate (IV) over Adams catalyst in acetic acid, only the phenyl group was reduced, giving the hexahydrobenzoate of the same alcohol. Ozonolysis of the decahydrobenzoate gave a compound which cyclised on working up, and the product was a carbonyl compound $C_{22}H_{24}O_3$, giving a dark red dinitrophenylhydrazone and having an absorption maximum at 1677 cm.$^{-1}$. The preparation was difficult to repeat, and we have no evidence to show which of the double bonds was split in this reaction.

Hydrogenation of the unsaturated ketone (I) over Raney nickel gave both 2α- and 2β-*cis*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-2-hydroxy-12-methylphenanthrene (VII) and (VIII); each is oxidised to the amorphous *cis*-ketone (IX). Birch reduction of the more plentiful 2α-hydroxy-compound (VII) was similar to that of the *trans*-isomer (II), the deca- and dodecahydro-phenanthrenes (X) and (XI) being obtained.

Reduction of *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-2β-hydroxy-6-methoxy-12-methylphenanthrene (XIII) or the related unsaturated ketone (XII) with 30 equivalents of lithium or sodium in methanol and liquid ammonia gave, after acid hydrolysis, a crystalline unsaturated ketone, $C_{15}H_{22}O_2$, in about 20% yield. The usual course of Birch reduction would produce one of the isomers (XIV) or (XV), which fit the analytical data. We consider that epimerisation during the acid-treatment will yield a larger amount of the isomer in which the 14-hydrogen atom is *cis* to the angular methyl group, and we provisionally assign to this product the structure (XIV). The mother-liquors gave 4% of an isomer (isolated as its benzoate) to which we assign formula (XV). The remainder of

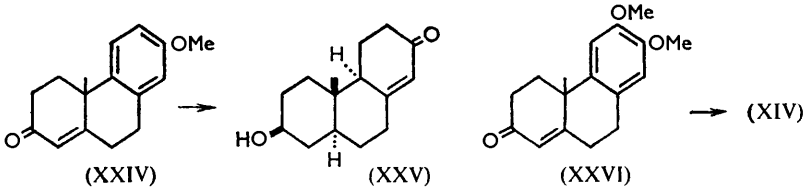
the reaction product was non-ketonic, and from it one crystalline compound (XVI) has been isolated. This contains one double bond, but is not identical with the isomer (alcohol from IV) obtained previously. It was not hydrogenated over palladised calcium carbonate, but over Adams catalyst in acetic acid gave the hexahydrobenzoate of a fully saturated alcohol. There is no evidence of the location of the double bond in this compound.

Further reduction of the unsaturated ketone (XIV) with sodium in liquid ammonia, or better hydrogenation over palladised calcium carbonate, gave a saturated ketone which we



consider to be the all-*trans*-isomer (XVII). This was not obtained entirely pure, for neither the benzoate nor the free alcohol was sharp-melting, and the dinitrophenylhydrazone was amorphous. With furfuraldehyde it gave the derivative (XVIII), which on ozonolysis gave a diacid, isolated as the crystalline acetate dimethyl ester (XIX).

Hydrogenation of the ketone (XII) over Raney nickel gave *cis*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-2α-hydroxy-6-methoxy-12-methylphenanthrene (XX). This was oxidised to the *cis*-ketone (XXI). Reduction of the *cis*-alcohol (XX) was similar to that of the *trans*-isomer, and gave a small yield of an unsaturated ketone (XXII) with, mostly, non-ketonic products from which an unsaturated benzoate (XXIII; R = Bz) was isolated. The location of the double bond in this compound is unknown, as is the full stereochemistry of the ketone (XXII).



Reduction of the ether (XXIV) gave a similar low yield of an unsaturated ketone, whose analysis agrees with the expected formula (XXV). We have also investigated the

reduction of the diether (XXVI): it gave a mixture from which only the ketone (XIV) was isolated.

Earlier we described [1] the ring extension of 1-methyl-2-tetralone by alkylation with 4-chlorobutan-2-one. This method, due to Walker,[2] has now been extended to the methoxy-derivatives. Uniformly good yields are obtained under suitable conditions. The preparation of the 6-methoxy-compound (XII) in this way is described below.

Experimental

trans-2β-*Benzoyloxy*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*decahydro*-12-*methylphenanthrene* (III).—To a solution of 2 : 3 : 4 : 9 : 10 : 12-hexahydro-12-methyl-2-oxophenanthrene (I) (1·0 g.) in dry methanol (100 ml.) and liquid ammonia (180 ml.) was added sodium (10 g.) in pieces during 20 min. After evaporation of the ammonia, water and ether were added, and the ether layer was washed and evaporated. Benzoylation of the residue and crystallisation from ethanol gave the *decahydro-compound benzoate* (1·1 g., 72%) as prisms, m. p. 137—139° (Found: C, 81·9; H, 8·2. $C_{22}H_{26}O_2$ requires C, 81·95; H, 8·1%). Hydrolysis gave an oily alcohol with no selective ultraviolet absorption.

Oxidation of this benzoate (100 mg.) in refluxing acetone (5 ml.) with potassium permanganate (100 mg.) gave the benzoate (II) (70 mg.) as needles, m. p. and mixed m. p. 160°.

trans-2β-*Benzoyloxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*dodecahydro*-12-*methylphenanthrene* (IV).—The benzoate (III) (200 mg.) in ethyl acetate (5 ml.) was shaken with hydrogen over palladised calcium carbonate. Filtration, evaporation, and crystallisation from ethanol gave the *dodecahydro-compound benzoate* (182 mg.) as plates, m. p. 118—121° (Found: C, 81·2; H, 8·5. $C_{22}H_{28}O_2$ requires C, 81·4; H, 8·7%). This was unaffected by permanganate in refluxing acetone.

Epoxidation of the Decahydro-compound Benzoate.—The benzoate (III) (200 mg.) was stirred in chloroform (6·0 ml.) with 90% formic acid (3·0 ml.) and 30% hydrogen peroxide (6·0 ml.) for 15 hr. Ether and water were added and the organic layer was washed and evaporated. The residue crystallised from ethanol, to give the *diepoxide* (V) (140 mg.) as prisms, m. p. 176—178° (Found: C, 74·8; H, 7·6. $C_{22}H_{26}O_4$ requires C, 74·55; H, 7·4%), having no infrared hydroxyl or ketone absorption.

Epoxidation of the Dodecahydro-compound Benzoate.—The benzoate (IV) (100 mg.) was epoxidised as above. Crystallisation from methanol gave the *monoepoxide* (VI) (70 mg.) as prisms, m. p. 120—122° (Found: C, 77·5; H, 8·25. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%).

Hydrogenation of the Dodecahydro-compound Benzoate.—The benzoate (IV) (100 mg.) in ether (5 ml.) and glacial acetic acid (5 ml.) was shaken with hydrogen over Adams catalyst. The product crystallised from ethanol to give the cyclo*hexanecarboxylate* (62 mg.) analogous to (IV), as prisms, m. p. 54—58° (Found: C, 80·35; H, 10·6. $C_{22}H_{34}O_2$ requires C, 79·95; H, 10·4%).

Ozonolysis of the Decahydro-compound Benzoate.—The benzoate (III) (200 mg.) in ethyl acetate (20 ml.) was ozonised at −60° until a permanent blue colour was obtained. The solvent was removed under reduced pressure, and the residue boiled with water (10 ml.) for 30 min. Ether-extraction gave an oil which crystallised from ethanol to give an unsaturated *ketone* (60 mg.) as prisms, m. p. 149—151° (Found: C, 78·8; H, 7·25. $C_{22}H_{24}O_3$ requires C, 78·5; H, 7·2%), $\nu_{max.}$ 1677 cm.$^{-1}$ in Nujol. The 2 : 4-*dinitrophenylhydrazone* formed dark red plates, m. p. 272—274°, from dioxan–ethanol (Found: C, 65·3; H, 5·4; N, 10·9. $C_{28}H_{28}O_6N_4$ requires C, 65·1; H, 5·5; N, 10·85%).

cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-2β-*hydroxy*-12-*methylphenanthrene* (VIII).—2 : 3 : 4 : 9 : 10 : 12-Hexahydro-12-methyl-2-oxophenanthrene (5·0 g.) in ethanol (100 ml.) was shaken with hydrogen over Raney nickel. After uptake of 2 mol. of hydrogen the solution was filtered and evaporated. The residue was benzoylated, giving the *cis*-2α-benzoate (5·2 g.), m. p. 150—154° (from ethanol), of the alcohol (VII). Concentration of the mother-liquor and crystallisation from ethanol gave the cis-2β-*benzoate* (1·45 g.) as plates, m. p. 96° (Found: C, 82·15; H, 7·6. $C_{22}H_{24}O_2$ requires C, 82·5; H, 7·55%). Alkaline hydrolysis gave the free cis-2β-*alcohol* (VIII), forming prisms, m. p. 69—70°, from light petroleum (b. p. 60—80°) (Found: C, 83·75; H, 9·6. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%).

[1] Howell and Taylor, *J.*, 1958, 1248.
[2] Walker, *J.*, 1935, 1585; cf. Robinson, *J.*, 1936, 1089.

Oxidation of the alcohol (VIII) as described for the cis-2α-isomer [1] gave the known *cis*-ketone (semicarbazone, m. p. 196—198°).

cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10 : 11 : 12-*Decahydro*-2α-*hydroxy*-12-*methylphenanthrene* (X).—The *cis*-2α-alcohol (VII) (1·5 g.) was reduced as described for the *trans*-series, with sodium (12 g.), methanol (100 ml.), and liquid ammonia (180 ml.). The *cis*-decahydro-2α-alcohol (1·2 g., 80%) formed needles, m. p. 87—89°, from light petroleum (b. p. 60—80°) (Found: C, 82·2; H, 10·2. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). The ultra-violet absorption spectrum showed no characteristic maximum. The derived *benzoate* formed plates, m. p. 106—108°, from ethanol (Found: C, 82·0; H, 8·1. $C_{22}H_{26}O_2$ requires C, 81·95; H, 8·1%). Both the alcohol and the benzoate readily formed mixed crystals of sharp melting point with the parent aromatic compounds.

cis-2-α-*Benzoyloxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*dodecahydro*-12-*methylphenanthrene*.—The above *cis*-decahydro-2α-benzoate (100 mg.) in ethyl acetate (5 ml.) was shaken with hydrogen over palladised calcium carbonate. Filtration and evaporation gave a residue which on crystallisation from ethanol gave the *benzoate* (80 mg.) as plates, m. p. 111—113° (Found: C, 81·5; H, 9·0. $C_{22}H_{28}O_2$ requires C, 81·4; H, 8·7%), of compound (XI).

2 : 3 : 4 : 9 : 10 : 12-*Hexahydro*-6-*methoxy*-12-*methyl*-2-*oxophenanthrene* (XII).—7-Methoxy-1-methyl-2-tetralone (32 g.) was dissolved in a solution from sodium (4·0 g.) and methanol (100 ml.), and the whole added during 1 hr. to 4-chlorobutan-2-one (20 g.) in methanol (100 ml.) with stirring under nitrogen. After a further 30 min. a solution from sodium (4·0 g.) and methanol (100 ml.) was added during 15 min., and the mixture stirred for 45 min. at room temperature and then for 30 min. at the b. p. After addition of dilute sulphuric acid and ether, the ether layer was washed and evaporated, and the residue distilled. A pale yellow oil (31·9 g.), collected at 185°/0·3 mm., crystallised on dilution with ether and light petroleum (b. p. 40—60°) to give the pure tricyclic ketone (21·1 g.), m. p. 62°. Chromatography of the mother-liquor gave a further amount (2·6 g., total 58%).

trans-2β-*Benzoyloxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-6-*methoxy*-12-*methylphenanthrene* (cf. XIII).—*trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-6-methoxy-12-methyl-2-oxophenanthrene [1] (100 mg.) in ethanol (10 ml.) was shaken with hydrogen over Adams catalyst. After filtration and evaporation the oily residue was benzoylated. The *benzoate* (110 mg.) formed colourless plates, m. p. 141—142°, from ethanol (Found: C, 78·5; H, 7·6. $C_{23}H_{26}O_3$ requires C, 78·8; H, 7·5%).

1 : 2 : 3 : 4 : 6 : 7 : 8 : 9 : 10 : 11α : 12 : 14β-*Dodecahydro*-2β-*hydroxy*-12-*methyl*-6-*oxophenanthrene* (XIV).—(*A*) *trans*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-Octahydro-2β-hydroxy-6-methoxy-12-methylphenanthrene (XIII) (2·5 g., from reduction of the ketone by lithium aluminium hydride) in ether (100 ml.) was added to liquid ammonia (300 ml.) containing lithium (0·5 g.). Methanol was added dropwise until the blue colour disappeared. More lithium (3 × 0·5 g.) was then added, and the colour discharged with methanol each time. After evaporation of the ammonia, ether and water were added, the ether layer was evaporated, and the residue refluxed for 3 hr. with ethanol (150 ml.), water (25 ml.), and concentrated hydrochloric acid (25 ml.). The oil isolated with ether was chromatographed on alumina (100 g.) in benzene. Benzene containing chloroform (10%) eluted an oil, crystallising from ether to give the *keto-alcohol* (0·5 g.) as yellow prisms, m. p. 118—120° (Found: C, 76·6; H, 10·0. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%), $\lambda_{max.}$ (in EtOH) 239 mμ (log ε 4·08), $\nu_{max.}$ (in Nujol) 1650, 3421 cm.$^{-1}$. The 2 : 4-*dinitrophenylhydrazone* formed red plates, m. p. 236—237° (decomp.), from dioxan–ethanol (Found: C, 60·9; H, 6·3; N, 13·3. $C_{21}H_{26}O_5N_4$ requires C, 60·85; H, 6·3; N, 13·5%). Crystallisation of this from acetic acid gave the *dinitrophenylhydrazone acetate* as dark red prisms, m. p. 239—241° (decomp.) (Found: C, 60·2; H, 6·1; N, 11·9. $C_{23}H_{28}O_6N_4$ requires C, 60·5; H, 6·2; N, 12·3%). The *ketone benzoate* formed plates, m. p. 174—175°, from methanol (Found: C, 78·0; H, 8·0. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%); acid-hydrolysis regenerates the alcohol, but alkali causes resinification.

(*B*) 2 : 3 : 4 : 9 : 10 : 12-Hexahydro-6-methoxy-12-methyl-2-oxophenanthrene (XII) (2·5 g.) was reduced with sodium (12 g.) and methanol (125 ml.) in liquid ammonia (200 ml.) as described for the preparation of compound (III). The product, afteracid-hydrolys is as in method (*A*), was chromatographed on alumina (100 g.). Benzene and benzene containing chloroform (10%) eluted a non-ketonic oil, which after benzoylation crystallised from ethanol to give 2β-*benzoyloxy*-1 : 2 : 3 : 4 : x : x : x : x : 9 : 10 : 11 : 12-*dodecahydro*-12-*methylphenanthrene* (XVI) (345 mg.) as prisms, m. p. 113—116° (Found: C, 81·5; H, 9·0. $C_{22}H_{28}O_2$ requires C, 81·5; H, 8·7%). Benzene containing chloroform (20%) gave first the isomeric 14α-keto-alcohol (XV), isolated as

its *benzoate* (140 mg.); this crystallised from methanol in prisms, m. p. 174—175°, giving a strong depression with its isomer (Found: C, 78·1; H, 7·9. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%), $\lambda_{max.}$ (in EtOH) 241 mμ (log ε 3·87), $\nu_{max.}$ (in Nujol) 1667 cm.$^{-1}$. The infrared spectrum was very similar to that of the isomer. Further elution with benzene containing chloroform (20%) gave the 14β-keto-alcohol (410 mg.), crystallising from ether in yellow prisms, m. p.118—120°, identical with the previous sample. Benzoylation of the mother-liquors gave the 14β-keto-benzoate (35 mg.), m. p. and mixed m. p. 174—175°.

Hydrogenation of the Dodecahydro-compound Benzoate (cf. XVI).—Hydrogenation over Adams catalyst in acetic acid gave the completely hydrogenated 2β-cyclo*hexanecarbonyloxyperhydro*-12-*methylphenanthrene* which crystallised from ethanol in plates, m. p. 66—68° (Found: C, 79·0; H, 10·95. $C_{22}H_{36}O_2$ requires C, 79·5; H, 10·9%).

Hydrogenation of the 14β-*Keto-alcohol* (XVI).—This keto-alcohol (250 mg.) in ethanol (10 ml.) was shaken with hydrogen over palladised calcium carbonate. The solution was filtered and evaporated, the residue crystallised from ether to give the *saturated keto-alcohol* (XVII) (100 mg.) as prisms, m. p. 98—102° (Found: C, 76·5; H, 10·0. $C_{15}H_{24}O_2$ requires C, 76·2; H, 10·1%). The *dinitrophenylhydrazone* was an amorphous orange solid, m. p. 180—220° (Found: C, 60·5; H, 6·6; N, 13·0. $C_{21}H_{28}O_5N_4$ requires C, 60·6; H, 6·8; N, 13·45%). The *benzoate* formed prisms, m. p. 175—177°, from methanol (Found: C, 77·7; H, 8·6. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%).

trans-anti-trans-7-*Furfurylideneperhydro*-2-*hydroxy*-6-*oxophenanthrene* (XVIII).—The ketone (XVII) (120 mg.) in methanol (3·0 ml.) was kept overnight under nitrogen with 33% sodium hydroxide solution (2·0 ml.) and furfuraldehyde (100 mg.). Ether and water were added, and the organic layer was washed neutral and evaporated. The residue crystallised from methanol to give the *furfurylidene-ketone* (80 mg.) as yellow prisms, m. p. 197—207° (Found: C, 76·1; H, 8·3. $C_{20}H_{26}O_3$ requires C, 76·4; H, 8·3%), $\nu_{max.}$ (in Nujol) 1673 cm.$^{-1}$.

6β-*Acetoxy*-1β : 2α-*di*(*methoxycarbonylmethyl*)-9β-*methyl*-trans-*decalin* (XIX).—The above furfurylidene derivative (140 mg.) was acetylated and then ozonised at −80° in ethyl acetate (20 ml.) until a strong blue colour persisted. The solvent was evaporated under reduced pressure, and acetic acid (10 ml.), water (2·5 ml.) and 30% hydrogen peroxide (1·0 ml.) were added. After being kept overnight the whole was extracted with ether, and the extract washed and evaporated. The residue was esterified with diazomethane, and then crystallised from methanol to give the *acetate dimethyl ester* (129 mg.) as prisms, m. p. 103° (Found: C, 64·5; H, 8·7. $C_{19}H_{30}O_6$ requires C, 64·4; H, 8·5%). The *benzoate diacid* crystallised from methanol in prisms, m. p. 277° (Found: C, 66·9, 67·0; H, 7·5, 7·4; O, 25·0. $C_{22}H_{28}O_6$ requires C, 68·0; H, 7·3; O, 24·7%).

cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-2α-*hydroxy*-6-*methoxy*-12-*methylphenanthrene* (XX).—2 : 3 : 4 : 9 : 10 : 12-Hexahydro-6-methoxy-12-methyl-2-oxophenanthrene (XII) (300 mg.) in ethanol (10 ml.) was shaken with hydrogen over Raney nickel. After filtration and evaporation the residue was benzoylated. Crystallisation from ethanol gave the cis-2α-*benzoate* (260 mg.) as prisms, m. p. 117—119° (Found: C, 78·7; H, 7·8. $C_{23}H_{26}O_3$ requires C, 78·8; H, 7·5%). Alkaline hydrolysis gave the free *alcohol*, crystallising from light petroleum (b. p. 60—80°) in needles, m. p. 98—100° (Found: C, 77·9; H, 9·3. $C_{16}H_{22}O_2$ requires C, 78·0; H, 9·0%).

cis-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*Octahydro*-6-*methoxy*-12-*methyl*-2-*oxophenanthrene* (XXI).—The *cis*-alcohol (200 mg.) in acetone (5 ml.) was oxidised by the procedure of Bowers *et al.*[3] Crystallisation from light petroleum (b. p. 60—80°) gave the cis-*ketone* (187 mg.) as prisms, m. p. 79—81° (Found: C, 78·3; H, 8·0. $C_{16}H_{20}O_2$ requires C, 78·65; H, 8·25%).

cis-2α-*Benzoyloxy*-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9 : 10 : 11 : 12 : 14-*dodecahydro*-12-*methyl*-6-*oxophenanthrene* (cf. XXII).—The above *cis*-2α-alcohol (2·0 g.) was reduced with sodium (10 g.) in methanol (100 ml.) and liquid ammonia (180 ml.) as described above. After hydrolysis the crude product was chromatographed on alumina (100 g.). Benzene containing chloroform (20%) eluted an oil which after benzoylation crystallised from methanol, to give a 2-α-*benzoyloxydodecahydro*-12-*methylphenanthrene* (XXIII) (390 mg.) as plates, m. p. 102—104° (Found: C, 81·6; H, 8·8. $C_{22}H_{28}O_2$ requires C, 81·4; H, 8·7%). Further elution with the same mixture gave an impure isomer (170 mg.), crystallising from methanol in plates, m. p. 108—112° (Found: C, 81·5; H, 8·4%). Elution with benzene containing more chloroform (50%) gave an oil which after benzoylation crystallised from methanol to give the *keto-benzoate* (cf. XXII) (200 mg.) as

[3] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

prisms, m. p. 124—126° (Found: C, 77·8; H, 8·1. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%), $\lambda_{max.}$ (in EtOH) 240 mμ (log ε 4·17), $\nu_{max.}$ (in Nujol) 1667 cm.$^{-1}$.

1 : 2 : 3 : 4 : 5 : 6 : 7 : 9 : 10 : 11α : 12 : 13α-*Dodecahydro*-2β-*hydroxy*-12-*methyl*-7-*oxophenanthrene* (XXV).—2 : 3 : 4 : 9 : 10 : 12-Hexahydro-7-methoxy-12-methyl-2-oxophenanthrene (XXIV) (1·0 g.) was reduced with sodium (5 g.) in methanol (50 ml.) and liquid ammonia (90 ml.) as usual. After acid-hydrolysis, the product was chromatographed on alumina (50 g.). Elution with benzene containing chloroform (5—20%) gave a middle fraction that crystallised from ether, to give the *keto-alcohol* (32 mg.) as yellow prisms, m. p. 122—124° [Found: C, 76·9; H, 9·3. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%), $\lambda_{max.}$ (in EtOH) 241 mμ (log ε 3·59)]. Benzoylation of material from the mother-liquors and crystallisation from methanol gave the *benzoate* of the same alcohol (133 mg.) as needles, m. p. 175° (Found: C, 77·7; H, 7·95. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%). Benzoylation of the crystalline alcohol gave the same substance.

Reduction of 2 : 3 : 4 : 9 : 10 : 12-*Hexahydro*-6 : 7-*dimethoxy*-2-*oxophenanthrene* (XXVI).—This ketone (2·05 g.) was reduced with sodium (15 g.) in methanol (100 ml.) and liquid ammonia (180 ml.). After acid-hydrolysis the product was chromatographed on alumina (100 g.). Benzene containing chloroform (50%) eluted an oil which on benzoylation gave the keto-benzoate (cf. XIV) (150 mg.), crystallising from methanol in plates, m. p. 174—175° undepressed with the previous specimen, and having an identical infrared spectrum.

THE UNIVERSITY, LIVERPOOL.
UNIVERSITY COLLEGE, IBADAN, NIGERIA.

[*Received, December 9th*, 1958.]