Studies on the Diels–Alder Reaction. Part III. The Stereochemistry of Perhydro-1 : 4-dioxophenanthrene and Related Compounds.*

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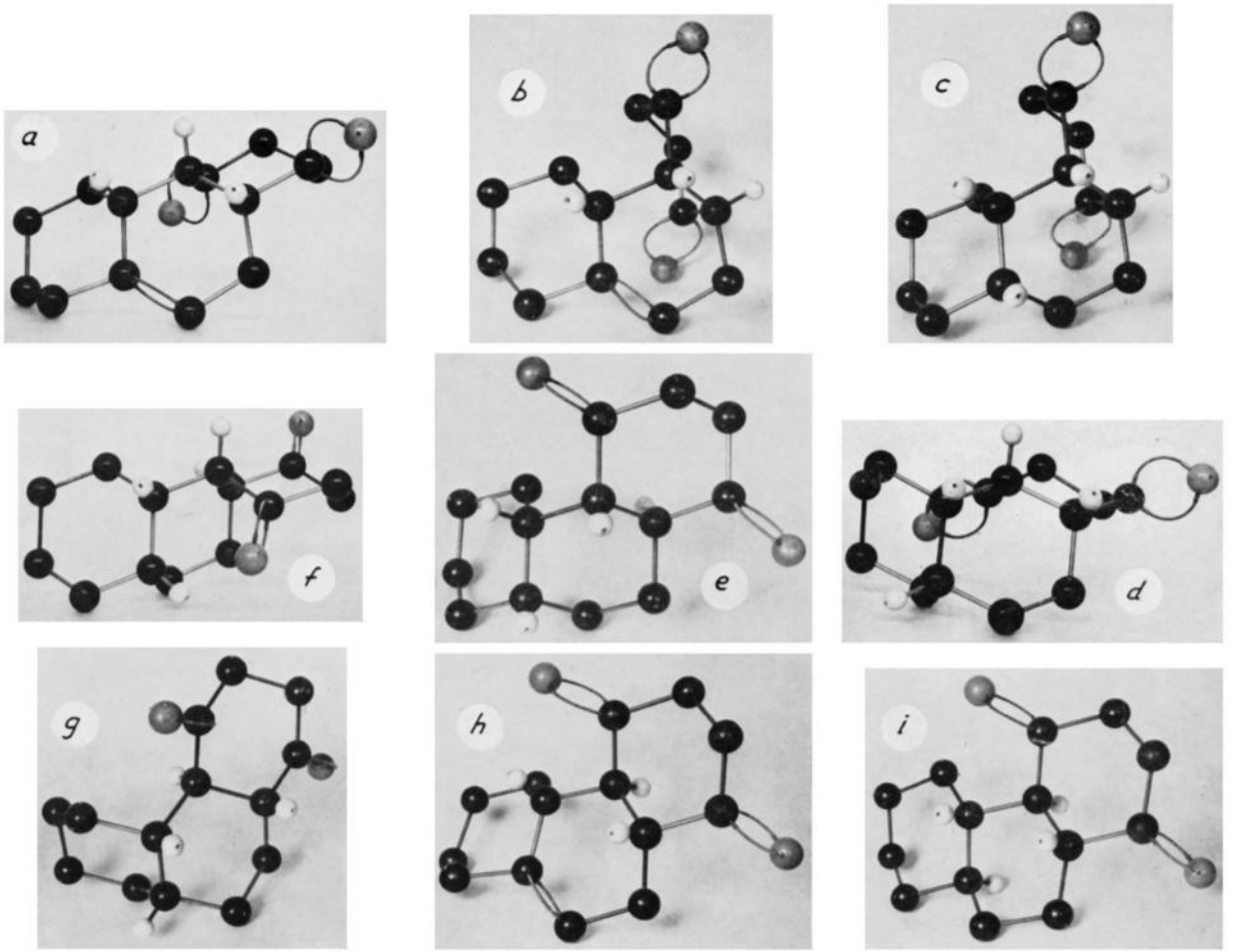
Starting from the stereochemically unstable *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I), selective methods of reduction and oxidation, together with controlled stereochemical inversions at points of ring-fusion rendered labile by the presence of adjacent carbonyl groups, have given access to a series of five perhydro-1 : 4-dioxophenanthrenes and related hydroxyketones. Interconversions by way of characterised intermediates have made possible a logical assignment of structures to these stereoisomers, based on current views concerning the stereochemistry of the *cyclo*hexane ring and related fused ring systems, and provide experimental evidence for the following stability sequence for the five perhydro-1 : 4-dioxophenanthrenes and related hydroxyketones : *trans-anti-trans* > *trans-syn-cis* > *cis-anti-cis* > *trans-anti-cis* > *cis-syn-cis*.

On the basis of the now well-accepted premises that the *cyclo*hexane ring is significantly more stable in the chair than in the boat form and that substituents on the ring are more stable in the equatorial than in the axial conformation (cf. Hassel, *Research*, 1950, **3**, 504), Johnson (*Experientia*, 1951, **7**, 315) has suggested, assuming all three rings to have the chair conformation, that the relative stabilities of perhydrophenanthrenes should follow the order: *trans-anti-trans* > *trans-syn-cis* = *trans-anti-cis* > *cis-anti-cis* > *cis-syn-cis*. Following Turner's treatment of *trans-* and *cis*-decalin (*J. Amer. Chem. Soc.*, 1952, **74**, 2118), which, in good agreement with experiment, were estimated to differ from each other in energy by 2·4 kcal. owing to three skew interactions, Johnson (*ibid.*, 1953, **75**, 1498) has, further, assigned energy differences to the perhydrophenanthrenes on the basis of 0·8 kcal. per skew interaction (Pitzer, *Chem. Reviews*, 1940, **27**, 39; Becket, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488) as follows : *trans-anti-trans*, 0; *trans-syn-cis* and *trans-anti-cis*, 2·4 kcal.; *cis-anti-cis*, 4·0 kcal.; and *cis-syn-cis*, *ca.* 6·4 kcal. The *trans-syn-trans*-conformation is incapable of existing with the central ring (ring B) in the chair form and the energy difference for this form must exceed 5·6 kcal., the energy difference between the chair and the boat form of *cyclo*hexane (Becket *et al.*, *loc. cit.*). As we had ready access to *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I) (Part I, *J.*, 1952, 642), we were in a favourable position to demonstrate, by suitable choice of experimental conditions, a stability sequence of the above nature, the configuration of (I) being assigned on the sole basic assumptions (i) that the course of the Diels–Alder reaction between vinyl*cyclo*hexene and benzoquinone followed the Alder rules for diene additions (Alder and Stein, *Angew. Chem.*, 1937, **50**, 510), and (ii) that the mild conditions used for the reduction of the 2 : 3-double bond in the resulting *cis-syn*-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene (II) with zinc powder and glacial acetic acid had caused no stereochemical change at position(s) 11 and/or 12. Fortunately the reaction between vinyl*cyclo*hexene and benzoquinone was relatively rapid and there can be no doubt that (II) had the *cis-syn*-structure, but stereoisomerisation of the adduct initially formed may occur in slower diene-addition reactions of this type (cf. Lukes, Poos, and Sarett, *J. Amer. Chem. Soc.*, 1952, **74**, 1402); it may be stated now, however, that the above assumptions seem to have been fully justified and that the results to be described below do not appear to be capable of interpretation on any other basis. The 9(14)-position of the double bond in (I) was demonstrated by the presence in its infrared absorption spectrum of a strong band at 816 cm.$^{-1}$.

We have previously described (Part I) the catalytic hydrogenation of *cis-syn*-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene (II) over palladised strontium carbonate to a perhydro-1 : 4-dioxophenanthrene, m. p. 108—109° [also obtained on hydrogenation of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I) under mild conditions], to which the *cis-syn-*

* Part II, *J.*, 1952, 1610.



a, *b*: cis-syn-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dioxophenanthrene* (I).
c, *d*: cis-syn-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (III).
e: trans-syn-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (V).
f: cis-anti-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (XII).
g: trans-anti-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (XIII).
h: trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dioxophenanthrene* (XXI).
i: trans-anti-trans-*Perhydro*-1 : 4-*dioxophenanthrene* (XXIII).

For the sake of clarity hydrogen atoms are only shown at the points of ring fusion.

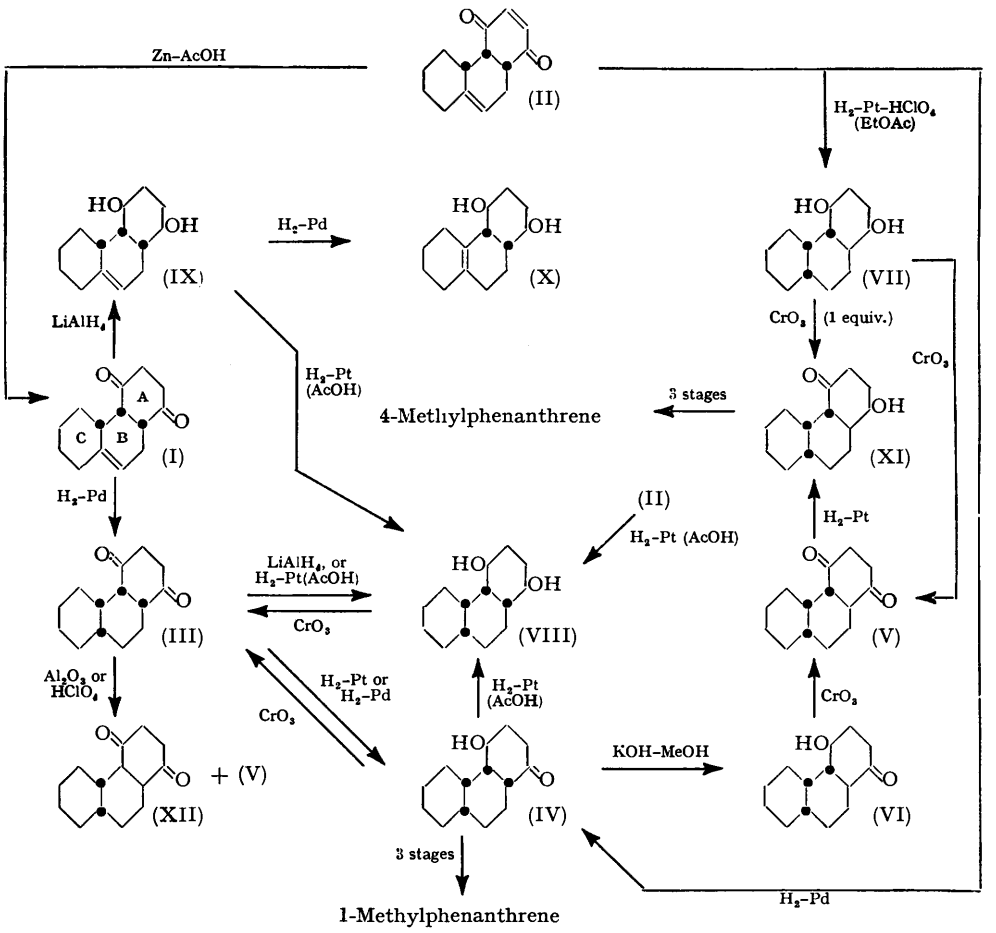
[*To face p.* 3961.

trans-structure was provisionally assigned, with the implication, which we pointed out, that ring A would not have interfered with the hydrogenation of the 9(14)-double bond in (I) by catalyst hindrance (cf. Linstead, Doering, Davis, Levine, and Whetstone, *ibid.*, 1942, **64**, 1985; Linstead and Whetstone, *J.*, 1950, 1428). In (I), carbon atoms $C_{(8)}$, $C_{(9)}$, $C_{(10)}$, $C_{(13)}$, and $C_{(14)}$ are coplanar because of the geometry of the double bond, and there are two possible conformations; in one of these (Fig. *a*) carbon atoms $C_{(1)}$, $C_{(4)}$, and $C_{(5)}$, considered as substituents of ring B, occupy respectively equatorial, axial, and quasi-equatorial positions, while in the other (Fig. *b*) the same substituents are respectively in axial, equatorial, and quasi-axial positions (for the terms " quasi-equatorial " and " quasi-axial," see Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21). The former conformation (Fig. *a*) is therefore the preferred one and it is favoured by experimental evidence to be described below, but both models (Fig. *a* and *b*) show ring A of (I) to be folded backwards roughly at right angles to the general plane of rings B and C in such a way as to cause quite marked catalyst hindrance, and the product of hydrogenation of (I) must therefore be *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone A) (III) (Fig. *c* or *d*), derived, theoretically, from the least stable of five (out of the six possible) perhydrophenanthrenes * and having carbonyl groups adjacent to, and rendering stereochemically labile, two points of ring fusion. Catalytic hydrogenation of (III) in acetic acid over Adams's platinum oxide catalyst and reduction with lithium aluminium hydride gave the same *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VIII), m. p. 134—135°, but hydrogenation in neutral solution gave a perhydro-4-hydroxy-1-oxophenanthrene, m. p. 138—139° (Part I), which retained the configuration of (III), since (III) resulted on oxidation with chromic acid, and which must therefore now be assigned the *cis-syn-cis*-structure (IV). The partial reduction of (III) to (IV) shows the 4-carbonyl group of (III) to be the less hindered, thus favouring the first of the two conformations shown (Fig. *c*) rather than the second (Fig. *d*). Treatment of the hydroxy-ketone (IV) with boiling 1% methanolic potassium hydroxide gave a stereoisomeric hydroxy-ketone, m. p. 141—142°, which could have been due either to inversion at $C_{(11)}$, as we had previously suggested, or, as kindly suggested by Professor W. S. Johnson (personal communication), to epimerisation at $C_{(4)}$, the latter being the more probable alternative on the basis of *cis-syn-trans*-structures for the above perhydro-1 : 4-dioxophenanthrene (diketone A) and perhydro-4-hydroxy-1-oxophenanthrene, m. p. 138—139°, although the conditions used in the alkaline stereoisomerisation were relatively mild. The latter alternative was excluded and the former verified, however, by an experiment, of which the significance had also been noted independently by Professor Johnson, namely, the oxidation of the hydroxy-ketone, m. p. 141—142°; this gave a diketone (diketone B), which was distinct from diketone A and must therefore have been the more stable *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (V) (Fig. *e*), and the hydroxy-ketone, m. p. 141—142°, was therefore *trans-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (VI). Diketone B was identical with the diketone obtained by oxidation with chromium trioxide of the perhydro-1 : 4-dihydroxyphenanthrene, m. p. 212° (VII), obtained by exhaustive hydrogenation of *cis-syn*-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene (II) over Adams's platinum oxide catalyst in ethyl acetate in the presence of perchloric acid (Part I), and, obviously, inversion at $C_{(11)}$ had occurred during the catalytic hydrogenation of (II) to (VII). This observation throws some light on the variable yields of *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VIII) (isolated as the dibenzoate) obtained when (II) was hydrogenated over Adams's platinum oxide catalyst in acetic acid in presence of a trace of perchloric acid (Part I), and treatment with perchloric acid was subsequently carried out deliberately as a test for stereochemical stability in ketones described in the present communication.

Reduction of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I) with lithium

* It may be noted that the six possible perhydrophenanthrenes can give rise theoretically to eight distinct optically inactive 1 : 4-dioxo-derivatives, since *trans-syn-cis-* and *trans-anti-cis*-perhydrophenanthrene can both give rise to two perhydro-1 : 4-dioxophenanthrenes, depending upon whether the *cis-* or the *trans*-fused side-ring bears the two carbonyl groups. No derivative of *trans-syn-trans*-perhydrophenanthrene was encountered in this investigation and no further reference will be made to this structure.

aluminium hydride gave *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX), which gave only a monobenzoate and a monotoluene-*p*-sulphonate in contrast with *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VIII) which readily gave a dibenzoate (Part I). Attempted catalytic hydrogenation of (IX) over palladised strontium carbonate resulted



in a negligible uptake of hydrogen and migration of the double bond to an inert position to give a substance, presumably *cis*-Δ^{13}-dodecahydro-1 : 4-dihydroxyphenanthrene (X), showing no infra-red absorption band at ~820 cm.$^{-1}$ characteristic of a trisubstituted ethylene. Double-bond migrations of a similar nature under hydrogenation conditions have been observed amongst unsaturated steroids (cf. Fieser and Fieser, " Natural Products related to Phenanthrene," Reinhold Publ. Corpn., New York, 1949, pp. 240, 249, 624; Rosenkranz, Romo, Batres, and Djerassi, *J. Org. Chem.*, 1951, **16**, 300), and hydrogenation of (IX) in acetic acid in presence of Adams's platinum oxide catalyst gave (X) and *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VIII) as major products, while minor products may have resulted from further shifts of the double bond, as observed in steroids (cf. Fieser and Fieser, *op. cit.*). The formation of (VIII) from (IX) in the latter hydrogenation shows these two compounds to share the same configurations at $C_{(1)}$ and $C_{(4)}$, a point of interest in relation to their behaviour towards oxidation which will be discussed later. On the basis of the preferred conformation (Fig. *a*) for *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I) one would expect the 4-hydroxyl group of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX), being produced in the reduction of a hindered carbonyl

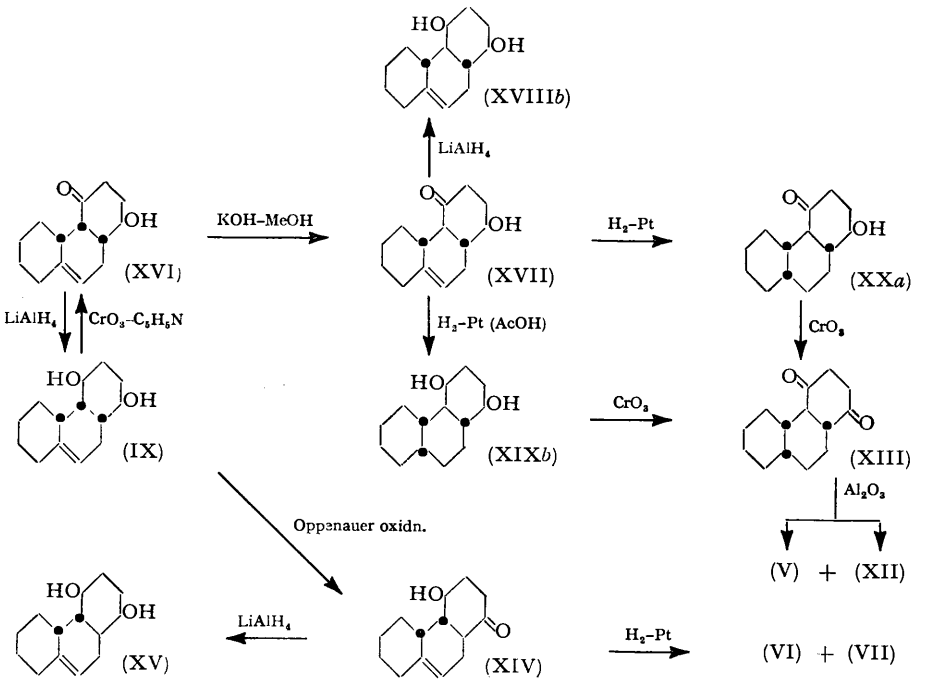
group, to occupy the axial position, and the 1-hydroxyl group to be equatorial, since it arises by reduction of an unhindered carbonyl group. From this line of reasoning it follows that the two hydroxyl groups in (IX) are in *trans*-position to the adjacent bridgehead hydrogen atoms and in *cis*-relation to each other, in agreement with relations experimentally established for the analogous reduction with lithium aluminium hydride of *cis*-6-ethoxy-Δ^6-octahydro-5-methyl-1 : 4-dioxonaphthalene (Beyler and Sarett, *J. Amer. Chem. Soc.*, 1952, **74**, 1406).

Hydrogenation of *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone B) (V) under mild conditions over Adams's platinum oxide catalyst gave a hydroxy-ketone, m. p. 173—174°, which, as it could be converted by marking the position of the carbonyl group with methylmagnesium iodide followed by dehydration and dehydrogenation into 4-methylphenanthrene, must have been *trans-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XI), isomeric with (VI), indicating the 1-carbonyl group of diketone B (V) to be the less hindered (cf. Fig. *e*). The partial oxidation with one equivalent of chromic acid of *trans-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VII) to *trans-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XI) is doubtless due to the fact that the 4-hydroxyl group in (VII) has the axial configuration and that the 1-hydroxyl group is equatorial (cf. Barton, *Experientia*, 1950, **6**, 316; *J.*, 1953, 1027). As *trans-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XI) was recovered unchanged on treatment with hot 10% methanolic potassium hydroxide, it appears, in accordance with Johnson's stability sequence, to be more stable than the *cis-anti-cis*-structure, into which it would have passed.

Passage of *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone A) (III) in benzene–light petroleum over alkaline alumina, or treatment in ethyl acetate solution with a trace of perchloric acid, gave a mixture of two stereoisomeric diketones. One of these was identified as *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone B) (V), which has been discussed above, and it is formed from (III) by inversion at $C_{(11)}$. The other diketone (diketone C) was a new substance and might have been expected to be that formed from (III) by inversion at $C_{(12)}$, *i.e.*, to be *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (XIII) (Fig. *g*); this structure, however, was excluded by the unequivocal preparation of a different diketone (diketone D) having the *trans-anti-cis*-configuration, as described below, and diketone C must therefore have been the product resulting from inversion at both $C_{(11)}$ and $C_{(12)}$, namely *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (XII) (Fig. *f*). The *cis-anti-cis*-structure is considered by Johnson (*locc. cit.*) to be less stable than either the *trans-syn-cis*- or the *trans-anti-cis*-configuration, and we have already noted the stability to alkali of *trans-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XI). Diketone C, however, was also obtained, as will be described below, by treatment of *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone D) (XIII) with alkaline alumina, so that *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone C) (XII) should be considered as having somewhat greater stability than is predictable on a quasi-theoretical basis. As far as we are aware, diketone C is the first *cis-anti-cis*-perhydrophenanthrene derivative to be described (cf. Linstead and Whetstone, *loc. cit.*).

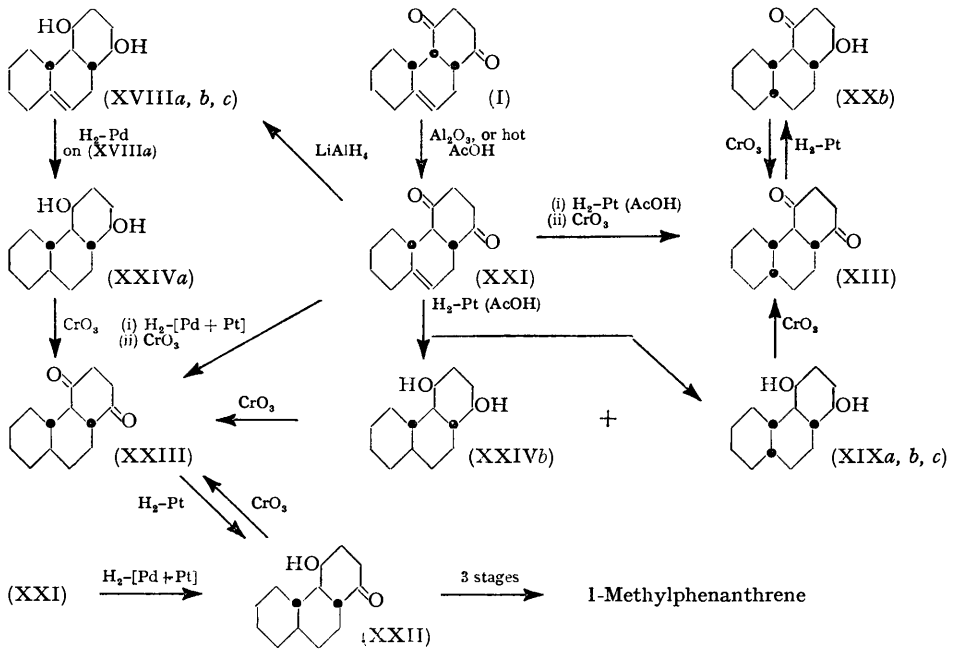
Whereas oxidation of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX) with chromium trioxide in acetic acid gave no recognisable product, the Oppenauer method afforded an unsaturated hydroxy-ketone, m. p. 126—128°, which gave on reduction with lithium aluminium hydride, not (IX), but a stereoisomeric unsaturated diol, m. p. 184—185°, indicating inversion to have taken place adjacent to the carbonyl group introduced during the Oppenauer oxidation in a similar fashion to that observed by Poos, Arth, Beyler, and Sarett (*J. Amer. Chem. Soc.*, 1953, **75**, 422) in an analogous case; furthermore, catalytic hydrogenation of the unsaturated hydroxy-ketone, m. p. 126—128°, over Adams's platinum oxide catalyst to give a mixture of *trans-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene

(VI) and *trans-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VII) showed it to be *trans-syn*-$\Delta^{9(14)}$-dodecahydro-4-hydroxy-1-oxophenanthrene (XIV), and the new unsaturated diol, m. p. 184—185°, obtained from it by reduction to be *trans-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (XV). As expected, the hydroxy-ketone (XIV), already equilibrated in the Oppenauer oxidation, was stable to methanolic potassium hydroxide. Oxidation of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX) with the chromium trioxide–pyridine reagent (cf. Poos *et al.*, *loc. cit.*) gave a new unsaturated hydroxy-ketone, m. p. 164—167°, shown to have retained the *cis-syn*-configuration by reduction with lithium aluminium hydride to its precursor (IX). It was unstable to alkali, however, and the product of stereoisomerisation was distinct from *trans-syn*-$\Delta^{9(14)}$-do-



decahydro-4-hydroxy-1-oxophenanthrene (XIV); obviously the chromium trioxide–pyridine reagent had effected oxidation at the secondary 4-alcohol group (cf. Poos *et al.*, *loc. cit.*), giving *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVI), which had passed on treatment with methanolic potassium hydroxide into the more stable *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII). The above stereospecific oxidations of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX), on the one hand at the secondary 1-alcohol group in the Oppenauer oxidation and, on the other, at the secondary 4-alcohol group with chromium trioxide–pyridine, are in agreement with the suggestion made above, on the basis of the preferred conformation for (I) (Fig. *a*), that the 1-hydroxyl group in (IX) is equatorial, while that at $C_{(4)}$ is axial; moreover, (IX) and (XVI) both gave a monobenzoate and a monotoluene-*p*-sulphonate, and acylation must have taken place at the unhindered 1-hydroxyl group. In contrast, *trans-syn*-$\Delta^{9(14)}$-dodecahydro-4-hydroxy-1-oxophenanthrene (XIV) did not react with toluene-*p*-sulphonyl chloride in pyridine in the usual way since in this substance only the axial 4-hydroxyl group is still present. Reduction of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII) with lithium aluminium hydride gave a *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene, m. p. 194—195° (XVIII*b*), but greater interest attached to the reduction of the 9 : 14-double bond. Catalytic hydrogenation over Adams's platinum oxide catalyst gave a hydroxy-ketone, m. p. 177—177·5°, in neutral solution, and a diol, m. p. 208—210°, in

glacial acetic acid, both of which passed on oxidation with chromic acid into the same new saturated diketone (diketone D). Equilibration of diketone D over alkaline alumina gave a mixture of diketone B and diketone C, together with unchanged diketone D. As diketone B has been shown to be *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (V), diketone D must also have a *cis*-fusion of rings B and C, and, as it was derived from *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII), it must have been *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (XIII) (Fig. *g*); the diol, m. p. 208—210°, and the hydroxy-ketone, m. p. 177—177·5°, were therefore *trans-anti-cis*-perhydro-1 : 4-dihydroxyphenanthrene (XIX*b*) and *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*a*) respectively. Diketones A, B, C, and D all have *cis*-fusion of rings B and C, and since the configurations of diketones A, B, and D are as derived above, diketone C must by exclusion,



as mentioned previously, be the remaining possibility, namely, *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (XII), for which the preferred conformation (Fig. *f*) has carbon atoms $C_{(4)}$ and $C_{(5)}$ as axial, rather than equatorial, substituents of ring B (cf. Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 1498).

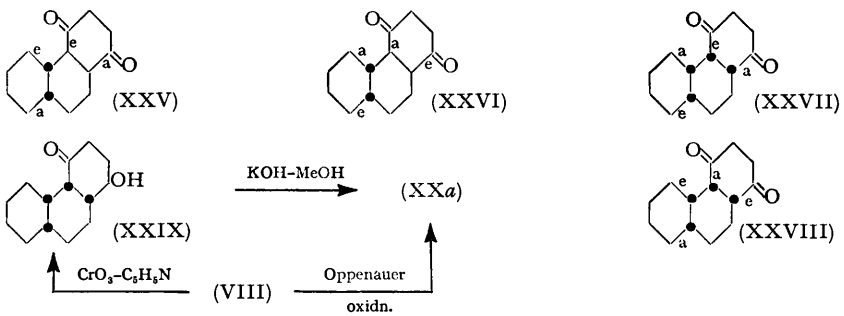
In Part I (*J.*, 1952, 642), a compound designated *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (XXI) was obtained in low yield when *cis-syn*-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene (II) was reduced with zinc powder in boiling acetic acid solution. The same substance was later obtained from *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I) in boiling acetic acid, again in low yield, or, in a practicable preparative yield (60—75%), by passing a benzene solution of (I) down a column of alkaline activated alumina under carefully controlled conditions. Subsequent reduction of the substance and the interrelations of the reduction products with each other and with other compounds described in the present communication have confirmed the above structure (XXI) (Fig. *h*). Reduction of (XXI) with lithium aluminium hydride afforded a mixture of diols which could be partially separated by fractional crystallisation and subsequently completely by chromatography on alumina to give three stereoisomeric *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrenes (XVIII*a*, *b*, *c*,), which can only differ with respect to the configurations at $C_{(1)}$ and $C_{(4)}$. One of these (XVIII*b*) was identical with the diol obtained by reduction of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII), which

must, from its mode of formation, have the *trans-anti*-structure. Catalytic hydrogenation of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (XXI) under neutral conditions in presence of a mixture of palladium and platinum catalysts gave a saturated hydroxy-ketone, m. p. 138—140°, and, on chromium trioxide oxidation of the material remaining in the mother-liquors, a new saturated diketone (diketone E), which were interconvertible by hydrogenation and oxidation with chromium trioxide in acetic acid. The hydroxy-ketone, m. p. 138—140°, was shown to be a perhydro-4-hydroxy-1-oxophenanthrene by marking the position of the carbonyl group with methylmagnesium iodide and conversion into 1-methylphenanthrene in the usual way (cf. Part I). As diketone D has been shown to be the *trans-anti-cis*-stereoisomer (XIII), the only remaining structure derivable from a *trans-anti*-$\Delta^{9(14)}$-precursor is the *trans-anti-trans*-one, and the hydroxy-ketone of m. p. 138—140° and diketone E must therefore be *trans-anti-trans*-perhydro-4-hydroxy-1-oxophenanthrene (XXII) and *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (XXIII) (Fig. *i*) respectively. In conformity with their expected maximal stability, the hydroxy-ketone (XXII) was recovered unchanged after treatment with boiling 10% methanolic potassium hydroxide or with potassium *tert.*-butoxide in boiling *tert.*-butanol, and diketone E (XXIII) was stable towards alkaline activated alumina, to dissolution in cold concentrated sulphuric acid and reprecipitation, and to dilute perchloric acid in ethyl acetate solution. Catalytic hydrogenation of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (XVIII*a*) over palladised strontium carbonate in methanol gave a perhydrodiol, m. p. 190—191°, which, as it gave diketone E on oxidation with chromium trioxide in acetic acid, must have been *trans-anti-trans*-perhydro-1 : 4-dihydroxyphenanthrene (XXIV*a*). Catalytic hydrogenation of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (XXI) over Adams's platinum oxide catalyst in acetic acid and oxidation of the resulting crude product gave *trans-anti-cis*-perhydro- 1: 4-dioxophenanthrene (diketone D) (XIII), but, in one experiment, a small proportion of *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (diketone E) (XXIII) was found in the mother-liquors, and a careful study was then made of the intermediate perhydrodiols formed in this hydrogenation. Chromatographic separation on partly deactivated alumina gave four distinct substances; three of these passed on oxidation with chromium trioxide in acetic acid into diketone D (XIII) and therefore had the *trans-anti-cis*-structure (XIX*a*, *b*, *c*), and the remaining one gave diketone E (XXIII) on oxidation and must have been the *trans-anti-trans*-compound (XXIV*b*). The second of these *trans-anti-cis*-perhydro-1 : 4-dihydroxyphenanthrenes, m. p. 211° (XIX*b*), obtained in this experiment was identical with that, m. p. 208—210°, obtained (above) on catalytic hydrogenation of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII), but the *trans-anti-trans*-compound, m. p. 194—195° (XXIV*b*), was distinct from the *trans-anti-trans*-perhydro-1 : 4-dihydroxyphenanthrene, m. p. 190—191° (XXIV*a*), obtained by catalytic hydrogenation of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (XVIII*a*).

trans-anti-cis-Perhydro-1 : 4-dioxophenanthrene (diketone D) (XIII) on mild catalytic reduction gave rise to a hydroxy-ketone, m. p. 144—145°, which was stable to 10% alcoholic alkali and reconvertible into diketone D by oxidation with chromium trioxide in acetic acid. This hydroxy-ketone differed from the *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*a*) obtained (above) by catalytic hydrogenation of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII), but inspection of a model of diketone D (Fig. *g*) indicates the greater likelihood of reduction taking place at the 1-carbonyl group than at the 4-carbonyl group; the hydroxy-ketone, m. p. 144—145°, will probably have, as (XX*a*) must have, a keto-group at $C_{(4)}$, and it is therefore considered to be *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*b*), the difference between the two compounds (XX*a* and *b*) being associated solely with differing configurations at $C_{(1)}$. In (XX*a*) the 1-hydroxyl group must be axial, being derived by the transformation of a known equatorial hydroxyl group in (XVI) during the conformational change involved in passing from *cis-syn-* (XVI) to *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII) and (XX*a*) (compare Fig. *a* with Fig. *h* and Fig. *g*), whereas in (XX*b*) the 1-hydroxyl group, formed in the hydrogenation under neutral conditions of an unhindered carbonyl group, would be expected to be equatorial.

As we have shown, each of the saturated diketones A (III), B (V), D (XIII), and E (XXIII), on catalytic hydrogenation under mild conditions in neutral solution gives rise exclusively to one hydroxy-ketone, and, for the hydroxy-ketones derived from diketones A, B, and E, the position of the remaining carbonyl group was determined by marking with methylmagnesium iodide, followed by dehydration and dehydrogenation to 1- or 4-methylphenanthrene. In this way *cis-syn-cis-* (diketone A) (III) and *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (diketone E) (XXIII) gave 1-methylphenanthrene, indicating greater ease of reduction at the 4-carbonyl group, while *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone B) (V) gave 4-methylphenanthrene, indicating greater ease of reduction at the 1-carbonyl group. The relative ease of catalytic reduction of carbonyl groups in these saturated diketones must obviously be primarily dependent on relative accessibility to the catalyst, and, conversely, relative resistance to catalytic reduction must be dependent upon relative degrees of steric hindrance. Barton has discussed the problem of steric hindrance of carbonyl groups in relation to the *trans*-A/B series of steroids, to the 18-*iso*oleanane group of triterpenoids, and to lanostane (*J.*, 1953, 1035), but the problem is not an easy one, particularly with *cis*-fused rings, and mixed *cis*- and *trans*-fused rings. Examination of models (Figure) is helpful when the preferred conformation for the parent saturated hydrocarbon can be readily selected by Johnson's rule (*Experientia*, 1951, **7**, 315), that, considering the peripheral rings as substituents of the central ring, the preferred conformation is the one giving the greater number of equatorial substituents to the central ring, assuming all rings to have the chair form. Although Johnson (*loc. cit.*) discussed only *saturated* fused six-membered ring systems, this type of selection has been illustrated above in choosing the preferred conformation (Fig. *a*) for *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I), in discussing the reduction of (I) with lithium aluminium hydride, and in interpreting the stereospecific oxidation of the resulting *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX) with the chromium trioxide–pyridine reagent and by the Oppenauer method. There is no ambiguity with *trans-syn-cis-* (diketone B) (V) (Fig. *e*), *trans-anti-cis-* (diketone D) (XIII) (Fig. *g*) and *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (diketone E) (XXIII) (Fig. *i*), but there are two possible conformations (XXV; XXVI) for *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone C) (XII) of which the latter (Fig. *f*) is favoured by energy considerations (cf. Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 1498). Alternatively, in diketones B, D, and E, one may consider rings A and B of the perhydrophenanthrene ring system as a *trans*-decalin system and apply the same treatment as one would apply to a *cyclo*hexane ring, since the *trans*-decalin ring system with both rings in the chair form has a clearly discernible equatorial plane and axial substituents are as clearly seen as they are in *cyclo*hexane itself (cf. Hassel, *Quart. Reviews*, 1953, **7**, 229). When diketone B (V) (Fig. *e*) is considered in this way, $C_{(5)}$ of the phenanthrene ring system is an axial substituent of rings A and B, considered as a *trans*-decalin, while $C_{(8)}$ of the phenanthrene ring system is an equatorial substituent; the reverse obtains with diketone D (XIII) (Fig. *g*), $C_{(5)}$ being the equatorial and $C_{(8)}$ the axial substituent. In diketone B the axial substituent is attached to the β-carbon atom relative to the 4-carbonyl group, which is therefore hindered as shown experimentally. In diketone D the axial substituent in the γ-position is relatively remote, but the model suggests that it could conceivably hinder as close an approach of the 4-carbonyl as that of the 1-carbonyl group to a catalyst. In the case of diketone E (XXIII) (Fig. *i*) the *trans-anti-trans*-conformation has, like *cyclo*hexane and *trans*-decalin, a clearly discernible general equatorial plane and, as there are no axial substituents apart from hydrogen atoms, no differentiation between the two carbonyl groups of diketone E is feasible on conformational grounds. The fact that preferential reduction takes place at the 4-carbonyl group on catalytic hydrogenation, as noted above, is doubtless, in this case, attributable to van der Waals forces favouring a closer approach of the 4-carbonyl group to the catalyst surface. *cis-syn-cis*-Perhydro-1 : 4-dioxophenanthrene (diketone A) (III), however, presents an interesting case, since there are two equally favoured conformations (derived theoretically from enantiomorphous parent hydrocarbons); in one of these (XXVII) (Fig. *c*), $C_{(4)}$ and $C_{(8)}$ are equatorial substituents of ring B, and in the other (XXVIII) (Fig. *d*) $C_{(1)}$ and $C_{(5)}$ are equatorial. As partial catalytic reduction of (III) gave *cis-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene the former

conformation (Fig. *c*) would appear to be favoured in (III), involving an eversion of the conformation of the molecule during the hydrogenation of the 9 : 14-double bond in passing from *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I) (Fig. *a*) to (III) (Fig. *c*). It must be assumed that the saturation of the 9 : 14-double bond, with consequent removal of its coplanarity constraints, confers mobility [in the sense (XXVII) ⇌ (XXVIII)] on the molecule as a whole, and the preferred conformation (XXVII) (Fig. *c*) of *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (III) is based purely on selection of the conformation which appears to offer the lesser hindrance to the 4-carbonyl group. Turning, however, to the corresponding diol, *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VIII), in which the configurations at $C_{(1)}$ and $C_{(4)}$ and the relations of the two hydroxyl groups to the adjacent bridgehead hydrogen atoms are the same as they are in *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX), since (IX) could be catalytically hydrogenated to give (VIII), a striking difference is at once apparent, as (VIII) readily formed a dibenzoate, whereas (IX) formed only a monobenzoate and monotoluene-*p*-sulphonate. If our argument concerning the stereochemistry of (IX) is correct, and it appeared to be justified by the stereospecific oxidations of (IX) with the chromium trioxide–pyridine reagent and by the Oppenauer method, then one or other of the hydroxyl groups in (VIII) should be axial if



(VIII) has a unique conformation but as both are readily benzoylated there would appear to be no preference for the conformation adopted by (VIII). Similarly, in contrast with the stereospecific oxidations of (IX), oxidation of (VIII) with the chromium trioxide-pyridine reagent and by the Oppenauer method proceeded non-stereospecifically. In both experiments the product consisted of hydroxy-ketonic and diketonic material. A hydroxy-ketone isolated directly from the chromium trioxide–pyridine oxidation product was *cis-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XXIX), since it gave on stereoisomerisation with alcoholic alkali the previously isolated *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*a*). Purification of the remainder of the product by chromatography on alumina afforded diketone B and diketone C, resulting from stereoisomerisation of primarily formed diketone A, while the hydroxy-ketone fraction yielded a further quantity of (XX*a*) and material giving strong presumptive evidence from its infra-red absorption spectrum for the presence of *trans-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (VI), arising by stereoisomerisation of *cis-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (IV). The product from the Oppenauer oxidation, purified by chromatography on alumina, again gave diketone B (V), diketone C (XII), and the hydroxy-ketone (XX*a*). The high proportion of (XX*a*) in the hydroxy-ketone fraction indicated that little of an isomeric perhydro-4-hydroxy-1-oxophenanthrene could have been present, but the formation of diketones indicated clearly the occurrence of the oxidation of both secondary alcohol groups.

The results obtained in the present work have clearly shown that the five stereoisomeric perhydro-1 : 4-dioxophenanthrenes and related hydroxy-ketones, which we have studied, fall into a stability sequence in which the *cis-syn-cis-* (III) and the *trans-anti-trans-* (XXIII) members are respectively the least and the most stable, with the *cis-anti-cis-* (XII), *trans-anti-cis-* (XIII), and *trans-syn-cis-* (V) members occupying intermediate positions. The formation of *trans-syn-cis-* (V) and *cis-anti-cis-* (XII) in the stereoisomerisation of *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (III) involved a single and a double inversion

respectively, but no trace was found of the product (XIII) which should have resulted from the possible alternative single inversion. Likewise, the stereoisomerisation of *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (XIII) gave (XII) and (V), again by single and double inversion respectively, but, in this instance, unchanged material (XIII) was also isolated. In both cases (III) and (XIII), however, the product resulting from the double inversion was obtained in the smaller proportion. Obviously the energy differences between *trans-syn-cis-* (V), *cis-anti-cis-* (XII), and *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (XIII) are small, but the resistance shown by *trans-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XI) towards alkaline stereoisomerisation points to the *trans-syn-cis-* being more stable than the *cis-anti-cis*-structure; it also points to the fact that *trans-syn-cis-* (V) is unlikely to be an intermediate in the formation of *cis-anti-cis-* (XII) during the stereoisomerisation of *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (III). In the following Table there are assembled the significant observations concerning the stability of the various stereoisomeric forms that have emerged from this work, together with the inferences to be drawn from them. One may conclude from these that the stability sequence for the five stereoisomeric perhydro-1 : 4-dioxophenanthrenes and related hydroxy-ketones, which we have studied is : *trans-anti-trans* > *trans-syn-cis* > *cis-anti-cis* > *trans-anti-cis* > *cis-syn-cis*. This sequence differs from Johnson's postulated sequence for the perhydrophenanthrenes in placing the *cis-anti-cis-* before the *trans-anti-cis*-member, and our reason for placing the two diketones in that order is based on the extent to which *trans-anti-cis-* (XIII) appeared to undergo conversion on alkaline alumina into a mixture of *trans-syn-cis-* (V) and *cis-anti-cis-*

Observation	Inference concerning stability
Complete conversion of (III) into (V) + (XII) ...	*trans-syn-cis, cis-anti-cis* > *cis-syn-cis*
Substantial conversion of (XIII) into (V) + (XII)	*trans-syn-cis, cis-anti-cis* > *trans-anti-cis*
Stability of (XXIII)	*trans-anti-trans* > *cis-anti-trans, cis-syn-trans,* (*trans-syn-trans*)
Conversion of (IV) into (VI)	*trans-syn-cis* > *cis-syn-cis*
Conversion of (XXIX) into (XX*a*)	*trans-anti-cis* > *cis-syn-cis*
Stability of (XI)	*trans-syn-cis* > *cis-anti-cis*
Stability of (XXII)	*trans-anti-trans* > *cis-anti-trans*
[Stability of (XX*b*)	*trans-anti-cis* > *cis-syn-cis*]

perhydro-1 : 4-dioxophenanthrene (XII). While Johnson's treatment may apply without reservations to the parent perhydrophenanthrenes, the introduction of carbonyl groups, as in the present series of compounds, may result in some stabilisation of boat forms (cf. Hassel, *Quart. Reviews*, 1953, **7**, 230), as is suggested by the dipole moment of *cyclo*hexane-1 : 4-dione (Le Fèvre and Le Fèvre, *J.*, 1935, 1696), which is unlikely to be due to enolisation (cf., however, Svirbely and Lander, *J. Amer. Chem Soc.*, 1950, **72**, 3756), and by comparison of the dipole moments of androstane- and *ætio*cholane-3 : 17-dione with the calculated values (Nace and Turner, *ibid.*, 1953, **75**, 4063). We are not, however, in a position to decide whether such considerations may, or may not, have a bearing on the relative stabilities of (XII) and (XIII).

Experimental

M. p.s given in the form " m. p. (micro) " were observed on a microscope hot stage, otherwise they were taken in capillary tubes in the usual way. In no case encountered in the present work did the m. p. of a mixture of non-identical substances, individually of similar m. p., fail to show a marked depression.

*Stability of Perhydro-*1 : 4-*dioxophenanthrenes and of Perhydro-*1(*or* 4)-*hydroxy-*4(*or* 1)-*oxophenanthrenes to Stereoisomeric Change.*—In order to demonstrate the stability, or otherwise, of various members of these series, at least one of the following tests was applied : (i) refluxing with 2% (or up to 10%) methanolic potassium hydroxide; (ii) passage down a column of alkaline alumina in a solvent of suitable eluting power; (iii) treatment at room temperature with a dilute solution of perchloric acid in ethyl acetate. The first of these tests was not applicable to the diketones, since, in every case, these substances rapidly gave brown decomposition products under alkaline conditions, possibly through enolisation and dehydrogenation. In the case of the *trans-anti-trans*-compounds more vigorous conditions were applied, as described later.

cis-syn-cis-*Perhydro-*1 : 4-*dihydroxyphenanthrene* (VIII).—A solution of *cis-syn-cis*-perhydro-

1 : 4-dioxophenanthrene (diketone A) (III) (500 mg.) in dry ether (50 c.c.) was added to a stirred solution of lithium aluminium hydride (1 g.) in dry ether (100 c.c.). The mixture refluxed spontaneously for a few seconds and it was then stirred at room temperature for 30 min. After cautious addition of 2N-sulphuric acid (50 c.c.) the ether layer was washed with water, dried, and evaporated, yielding a gum, which readily solidified when seeded with perhydro-1 : 4-dihydroxyphenanthrene, m. p. 134—135° (Part I). One recrystallisation from ethyl acetate–light petroleum gave colourless prisms (440 mg.), m. p. 132—133°, not depressed on admixture with the diol, m. p. 134—135°, obtained previously.

Catalytic reduction of *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone A) in acetic acid, with Adams's platinum oxide as catalyst, gave the same *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene in good yield, as did also *cis-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (IV).

Oxidation of cis-syn-cis-*Perhydro-4-hydroxy-1-oxophenanthrene* (IV) *to* cis-syn-cis-*Perhydro-1 : 4-dioxophenanthrene* (*Diketone* A) (III).—The hydroxy-ketone (IV) (Part I) (50 mg.) in acetic acid (5 c.c.) was treated with chromium trioxide (17 mg.) dissolved in a few drops of water. After being kept overnight at room temperature, the product was isolated in ether, and crystallisation from light petroleum gave clusters of needles, m. p. 109—110°, not depressed on admixture with *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone A) (III).

Oxidation of trans-syn-cis-*Perhydro-4-hydroxy-1-oxophenanthrene* (VI). trans-syn-cis-*Perhydro-1 : 4-dioxophenanthrene* (V).—The hydroxy-ketone (VI) (90 mg.), obtained by treatment of *cis-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (IV) with 1% methanolic potassium hydroxide (Part I), was treated in glacial acetic acid (10 c.c.) with chromium trioxide (60 mg., 2 equivs.) dissolved in a few drops of water. After being kept overnight at room temperature, excess of chromium trioxide was destroyed by addition of a few drops of methanol, the mixture was diluted with water, and the product was recovered in benzene. Crystallisation from light petroleum gave *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (V) (40 mg.), m. p. 115—116° (after drying in a vacuum at 80°), not depressed on admixture with the diketone (diketone B) obtained by oxidation of the perhydro-1 : 4-dihydroxyphenanthrene, m. p. 212° (Part I).

Reduction of cis-syn-$\Delta^{9(14)}$-*Dodecahydro-1 : 4-dioxophenanthrene* (I) *with Lithium Aluminium Hydride.* cis-syn-$\Delta^{9(14)}$-*Dodecahydro-1 : 4-dihydroxyphenanthrene* (IX).—*cis-syn-*$\Delta^{9(14)}$-Dodecahydro-1 : 4-dioxophenanthrene (5 g.) in dry ether (100 c.c.) was added to lithium aluminium hydride (5 g.) in dry ether (200 c.c.). After being heated under reflux for an hour, the reaction mixture was cooled, excess of lithium aluminium hydride was destroyed by dilute sulphuric acid, and the ethereal layer was separated, washed with water, dried, and evaporated. The resulting solid residue, on crystallisation from ethyl acetate–light petroleum, gave stout needles (3·7 g.) of cis-syn-$\Delta^{9(14)}$-*dodecahydro-1 : 4-dihydroxyphenanthrene* (IX), m. p. 127—128° (Found : C, 75·9; H, 10·0. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%), showing a strong band at 822 cm.$^{-1}$ and a weak band at 1650 cm.$^{-1}$ in its infra-red absorption spectrum.

The substance (0·85 g.) was treated in dry pyridine (10 c.c.) with toluene-*p*-sulphonyl chloride (1·6 g., 2·2 mols.). After the mixture had been kept at room temperature overnight the product was isolated with the aid of benzene to give an almost quantitative yield of the 1-*monotoluene-p-sulphonic* ester, m. p. 123—126°. Cautious recrystallisation from benzene–light petroleum with the minimum application of heat gave the pure ester in the form of prisms, m. p. 126—127° (Found : C, 67·2; H, 7·5. $C_{21}H_{28}O_4S$ requires C, 67·0; H, 7·5%). Similarly, benzoylation with excess of benzoyl chloride in pyridine gave the 1-*monobenzoate*, which crystallised from benzene–methanol in prisms, m. p. 133—134° (Found : C, 77·1; H, 8·3. $C_{21}H_{26}O_3$ requires C, 77·3; H, 8·0%).

Attempted Catalytic Hydrogenation of cis-syn-$\Delta^{9(14)}$-*Dodecahydro-1 : 4-dihydroxyphenanthrene* (IX). cis-Δ^{13}-*Dodecahydro-1 : 4-dihydroxyphenanthrene* (X).—(a) *With palladised strontium carbonate.* A solution of *cis-syn-*$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (200 mg.) in methanol (20 c.c.) was shaken in an atmosphere of hydrogen at room temperature and pressure in the presence of freshly reduced palladium–strontium carbonate (500 mg.). Absorption of hydrogen was negligible during 3 hr. On removal of the catalyst and evaporation of the solvent a solid residue was obtained. Extraction with boiling light petroleum left a small gummy residue which was not further investigated. The light petroleum solution, on cooling, deposited clusters of feathery needles (140 mg.), m. p. 105—106°, of an isomeric unsaturated diol; the substance gave a weak colour with tetranitromethane and, as it showed no absorption band in its infra-red absorption spectrum at *ca.* 820 cm.$^{-1}$ (characteristic of a trisubstituted ethylene), it was presumably cis-Δ^{13}-*dodecahydro-1 : 4-dihydroxyphenanthrene* (X) (Found : C, 75·4; H, 10·0. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

(b) *With Adams's platinum oxide catalyst.* A solution of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (2 g.) in glacial acetic acid (50 c.c.) was shaken in hydrogen at room temperature and pressure with Adams's catalyst (100 mg.). Absorption of hydrogen ceased after about 0·5 mol. had been taken up in 2 hr. A gum was obtained on removal of the catalyst and evaporation of the solvent. Chromatography on alumina (Savory & Moore Ltd.; partly deactivated by addition of 6% of water) in benzene gave, as the two major products, *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VIII) (0·4 g.), m. p. 132—134°, and the above *cis*-Δ^{13}-dodecahydro-1 : 4-dihydroxyphenanthrene (X) (0·65 g.), m. p. 105—106°. Two minor components, one crystallising from ethyl acetate–light petroleum in feathery needles, m. p. 210—211°, and one separating from the same solvent in nodules, m. p. 110—113°, were obtained, but in insufficient quantity for full characterisation; they were not, however, identical with any of the other saturated or unsaturated diols described in this paper.

trans-syn-cis-*Perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XI).—(a) *Hydrogenation of* trans-syn-cis-*perhydro*-1 : 4-*dioxophenanthrene* (diketone B) (V). Diketone B (200 mg.) was shaken in methanol (40 c.c.) in an atmosphere of hydrogen at room temperature and pressure with Adams's platinum oxide (50 mg.) until absorption of hydrogen ceased. Removal of the catalyst and solvent gave trans-syn-cis-*perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XI), which separated from ethyl acetate–light petroleum in colourless needles, m. p. 173—174° (Found : C, 75·6; H, 10·0. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

(b) *Partial oxidation of* trans-syn-cis-*perhydro*-1 : 4-*dihydroxyphenanthrene* (VII). *trans-syn-cis*-Perhydro-1 : 4-dihydroxyphenanthrene (200 mg.) in glacial acetic acid (30 c.c.) was oxidised overnight at room temperature with chromium trioxide (65 mg., 1·1 equiv.) dissolved in a few drops of water. The product, twice crystallised from benzene–light petroleum, gave *trans-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XI), m. p. 169—171°, not depressed on admixture with that obtained above.

The substance (XI) was recovered unchanged after 2 hours' refluxing with 10% methanolic potassium hydroxide.

Conversion of trans-syn-cis-*Perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XI) *to* 4-*Methylphenanthrene.—trans-syn-cis*-Perhydro-1-hydroxy-4-oxophenanthrene (1·15 g.) was treated in boiling benzene with methylmagnesium iodide (from 1·5 g. of magnesium) by the procedure outlined previously (Part I) for *cis-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (IV), except that purification of the product by means of Girard's reagent was not found necessary. The resulting trans-syn-cis-*perhydro*-1 : 4-*dihydroxy*-4-*methylphenanthrene* separated from ethyl acetate in fine colourless needles (0·82 g.), m. p. 205—206° (Found : C, 75·7; H, 11·0. $C_{15}H_{26}O_2$ requires C, 75·6; H, 11·0%). Dehydration by heating with potassium hydrogen sulphate and dehydrogenation with palladium–charcoal in boiling diphenylamine (cf. Part I) gave 4-methylphenanthrene (0·39 g.), which crystallised from methanol in plates, m. p. 51—52° (Found : C, 93·9; H, 6·6. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%). It formed a picrate, m. p. 142—143°, and a styphnate, m. p. 135—136°; Haworth (*J.*, 1932, 1125) records hydrocarbon, m. p. 49—50°, picrate, m. p. 140—141°, and styphnate, m. p. 135°.

Stereoisomerisation of cis-syn-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (*Diketone A*) (III). trans-syn-cis- (*Diketone B*) (V) *and* cis-anti-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (*Diketone C*) (XII).—(a) *With perchloric acid.* A solution of diketone A (200 mg.) in ethyl acetate (20 c.c.) was treated with perchloric acid (0·02 c.c. of 70%) and set aside at room temperature for 6 hr. After dilution with ether and washing with aqueous sodium hydrogen carbonate, the organic layer yielded, on evaporation, a gum which readily solidified on seeding with diketone B. Crystallisation from light petroleum gave woolly needles, m. p. 103—107°, and a further crystallisation from the same solvent gave a mixture of rosettes of fine needles and clusters of stout needles. After hand-sorting, the rosettes of fine needles gave, on crystallisation from light petroleum, *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone B) (V), m. p. 114—115°, not depressed on admixture with an authentic specimen, while the clusters of stout needles gave on recrystallisation a new stereoisomer, which, by exclusion, must have been cis-anti-cis-*perhydro*-1 : 4-*dioxophenanthrene* (diketone C) (XII), in the form of colourless plates, m. p. 139—141° (Found : C, 76·1; H, 9·4. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%).

(b) *With alkaline alumina.* Diketone A (0·5 g.) in benzene–light petroleum (1 : 4) was adsorbed on to a column of alkaline alumina (50 g.; Peter Spence & Sons, Ltd., type H). Fractional elution with benzene–light petroleum (1 : 1) gave fractions, all melting between 90° and 109°, recovery of material being virtually quantitative. A product of the same melting range was obtained on allowing a benzene solution of diketone A (0·2 g.) to percolate down a similar column of alumina and eluting it with benzene. The bulked fractions were crystallised from

light petroleum giving, as in (a), a mixture of rosettes of fine needles and clusters of long flattened needles. This mixture was separated by repeated hand-sorting and fractional crystallisation into diketone B, which crystallised in long needles or as rosettes of needles, m. p. 114—115°, not depressed on admixture with specimens obtained by alternative routes, and diketone C, identical with the material isolated in (a) and crystallising in flattened needles, or plates, m. p. 139—140°.

Oppenauer Oxidation of cis-syn-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dihydroxyphenanthrene* (IX). trans-syn-$\Delta^{9(14)}$-*Dodecahydro*-4-*hydroxy*-1-*oxophenanthrene* (XIV).—A solution of *cis*-*syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (3·35 g.) in benzene (150 c.c.) was refluxed for 8 hr. with *cyclo*hexanone (35 c.c.) and aluminium *iso*propoxide (3·5 g.). After cooling, water (7 c.c.) was added and the mixture was filtered. The filtrate was washed once with water and evaporated, finally at 130°/0·1 mm. The residue was triturated with benzene–light petroleum, and the resulting solid was collected. Recrystallisation from benzene–light petroleum gave trans-syn-$\Delta^{9(14)}$-*dodecahydro*-4-*hydroxy*-1-*oxophenanthrene* (XIV) (1·12 g.), m. p. 126—128°, depressed on admixture with the starting material (m. p. 127—128°) (Found : C, 76·4; H, 9·0. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%). Chromatography of the mother-liquors on alumina gave a further quantity of the same substance (XIV) (0·3 g.) and unchanged starting material (0·54 g.). The compound (XIV) was recovered unchanged after refluxing for an hour with 10% methanolic potassium hydroxide, and it failed to give a toluene-*p*-sulphonate under the usual conditions.

Reduction of (XIV) (300 mg.) in boiling ethereal solution with lithium aluminium hydride (500 mg.) for an hour, followed by decomposition of the mixture with excess of dilute sulphuric acid and isolation of the ether-soluble product, gave an unsaturated diol (200 mg.), crystallising from ethyl acetate in fine matted needles, m. p. 184—185°, and stereoisomeric with *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX); the following experiment showed it to be trans-syn-$\Delta^{9(14)}$-*dodecahydro*-1 : 4-*dihydroxyphenanthrene* (XV) (Found : C, 75·6; H, 10·0. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

Catalytic hydrogenation of the unsaturated hydroxy-ketone (XIV) (500 mg.) in methanol (50 c.c.) at room temperature and pressure in presence of Adams's platinum oxide (100 mg.) ceased after the absorption of approximately 1·2 mols. of hydrogen. Removal of the catalyst and solvent gave a solid residue. Crystallisation from benzene–light petroleum gave in poor yield rosettes of feathery needles, which, after two recrystallisations from ethyl acetate, had m. p. 208—210°, not depressed on admixture with *trans-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (VII). The mother-liquors on evaporation gave *trans-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (VI) (350 mg.), m. p. 141—142°, not depressed on admixture with a specimen obtained by an alternative route (Part I).

Oxidation of cis-syn-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dihydroxyphenanthrene* (IX) *with the Chromium Trioxide–Pyridine Reagent.* cis-syn- (XVI) *and* trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1-*hydroxy*-4-*oxophenanthrene* (XVII).—*cis-syn*-$\Delta^{9(14)}$-Dodecahydro-1 : 4-dihydroxyphenanthrene (1 g.) in pyridine (10 c.c.) was oxidised with the chromium trioxide–pyridine reagent (from 1·5 g. of chromium trioxide, 4·5 equivs., prepared according to Poos *et al.*, *loc. cit.*) in pyridine (20 c c.) at room temperature overnight. After addition of water and benzene, a flocculent brown precipitate was filtered off and washed well with benzene. The combined benzene solutions were washed free from pyridine with dilute mineral acid, then with water, and evaporated. Crystallisation of the residue from ethyl acetate afforded fine needles (0·54 g.) of cis-syn-$\Delta^{9(14)}$-*dodecahydro*-1-*hydroxy*-4-*oxophenanthrene* (XVI), m. p. 164—167° (Found : C, 76·2; H, 9·3. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%), showing a medium-intensity band at 820 cm.$^{-1}$ in its infrared absorption spectrum. The *benzoate*, obtained by the action of excess of benzoyl chloride in pyridine, separated from ethyl acetate–light petroleum in fine needles, m. p. 175—176° (Found : C, 77·7; H, 7·6. $C_{21}H_{24}O_3$ requires C, 77·8; H, 7·5%), and the *toluene*-p-*sulphonate* crystallised from aqueous methanol in plates, m. p. 137° (Found : C, 67·5; H, 7·3. $C_{21}H_{26}O_4S$ requires C, 67·4; H, 7·0%).

The substance (XVI) (200 mg.) in tetrahydrofuran (15 c.c.) was reduced with lithium aluminium hydride (200 mg.) under reflux for 1 hr. After destruction of excess of reagent with dilute sulphuric acid, the product was recovered by evaporation of the organic layer. Crystallisation from ethyl acetate–light petroleum gave prisms (130 mg.), m. p. 127—128°, not depressed on admixture with *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (IX).

The substance (XVI) (200 mg.) was heated under reflux for 2 hr. with 5% methanolic potassium hydroxide (20 c.c.). After cooling, dilution with water and recrystallisation of the precipated solid from light petroleum gave fine needles (140 mg.) of trans-anti-$\Delta^{9(14)}$-*dodecahydro*-

1-*hydroxy*-4-*oxophenanthrene* (XVII), m. p. 111—112° (Found: C, 76·2; H, 9·0. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%). Passage down a column of alkaline alumina in benzene–chloroform (4 : 1) solution failed to effect this stereoisomerisation, which was only partially effected by heating under reflux with 2% methanolic potassium hydroxide for 1 hr.

trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dihydroxyphenanthrene* (XVIII*b*).—A solution of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1-hydroxy-4-oxophenanthrene (XVII) (87 mg.) in dry ether was heated under reflux with lithium aluminium hydride (100 mg.) for 1 hr. After destruction of excess of reagent with ethyl acetate and decomposition of the mixture with excess of dilute sulphuric acid, the ether layer was separated, washed with water, dried, and evaporated. Crystallisation of the solid residue from ethyl acetate gave *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (XVIII*b*) (60 mg.), m. p. 194—195°, identical with a specimen prepared by an alternative route.

Catalytic Hydrogenation of trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1-*hydroxy*-4-*oxophenanthrene* (XVII).—(*a*) *trans-anti*-$\Delta^{9(14)}$-Dodecahydro-1-hydroxy-4-oxophenanthrene (170 mg.) was hydrogenated in methanol at atmospheric pressure and room temperature in presence of Adams's platinum oxide (50 mg.). Absorption of hydrogen was slow and appeared to cease entirely after about half the expected volume had been taken up. Removal of the catalyst and evaporation of the solvent gave a solid residue, which, on crystallisation from ethyl acetate–light petroleum, gave needles (63 mg.) of trans-anti-cis-*perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XX*a*), m. p. (micro) 177—177·5° (Found: C, 75·6; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%); oxidation of this compound (40 mg.) with chromium trioxide in acetic acid gave *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone D) (XIII), m. p. 107—109°, not depressed on admixture with an authentic specimen obtained as described below.

(*b*) *trans-anti*-$\Delta^{9(14)}$-Dodecahydro-1-hydroxy-4-oxophenanthrene (70 mg.) was hydrogenated in acetic acid (20 c.c.) at atmospheric pressure and room temperature in presence of Adams's platinum oxide until absorption ceased (1·5 hr.; 20 c.c.). After removal of the catalyst, evaporation of the solvent gave a solid residue, crystallising from ethyl acetate in fine needles, m. p. (micro) 208—210°, not depressed on admixture with a specimen of *trans-anti-cis*-perhydro-1 : 4-dihydroxyphenanthrene (XIX*b*), m. p. (micro) 211°, obtained as described below. Oxidation of this diol (XIX*b*) (60 mg.) in acetic acid (5 c.c.) with chromium trioxide (70 mg.) gave *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone D) (XIII) (30 mg.), m. p. 107—108°, not depressed on admixture with an authentic specimen (see below).

Stereoisomerisation of trans-anti-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (*Diketone* D) (XIII) *by Alkaline Alumina*.—A solution of diketone D (400 mg.) in benzene was allowed to percolate down a column of alumina (8 g., Peter Spence & Sons, Ltd., type H) and the column was eluted with benzene (300 c.c.). Evaporation of the eluate and exhaustive fractional crystallisation of the residue from light petroleum, combined with hand-sorting of the different crystalline forms obtained in many fractions, gave *trans-syn-cis*- (diketone B) (V) (100 mg.), m. p. 115—116°, *cis-anti-cis*- (diketone C) (XII) (140 mg.), m. p. 138—139°, and unchanged *trans-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone D) (XIII) (50 mg.), m. p. 109—110°, identical with authentic specimens.

Stereoisomerisation of cis-syn-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dioxophenanthrene* (I). trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dioxophenanthrene* (XXI).—A solution of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (1 g.) in benzene was allowed to percolate down a column of alkaline alumina (50 g., Peter Spence & Sons, Ltd., type H) and eluted with benzene. Evaporation of the eluate gave a solid residue (900 mg.), affording, after one recrystallisation from light petroleum, felted needles (600 mg.) of a stereoisomeric unsaturated diketone, namely *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (XXI), m. p. 139—140°, identical with that obtained in poor yield by reduction of *cis-syn*-$\Delta^{2:9(14)}$-decahydro-1 : 4-dioxophenanthrene (II) with zinc powder in boiling glacial acetic acid (Part I), or by boiling an acetic acid solution of *cis-syn*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (I). The substance (XXI) showed a medium-intensity band at 820 cm.$^{-1}$ in its infra-red absorption spectrum.

In a series of alkaline alumina stereoisomerisations of (I) carried out on a larger scale the yields were very variable; it was later found that a different specimen of alumina (Savory & Moore Ltd., " for chromatographic analysis ") gave more reproducible results on the larger scale (yields, 60—75%, with a ratio of compound to alumina of 1 : 20).

Reduction of trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dioxophenanthrene* (XXI) *with Lithium Aluminium Hydride*. trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dihydroxyphenanthrene* (XVIII*a*, *b*, *c*).—A solution of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (2 g.) in anhydrous ether (200 c.c.) was added to lithium aluminium hydride (3 g.) in ether (200 c.c.), and the mixture was

heated under reflux for 2 hr., then cooled and decomposed with cold dilute sulphuric acid. A quantity of insoluble solid was left in suspension and was collected by filtration (A), and the ether layer, after being washed with water, was dried and evaporated, giving a solid (B). Crystallisation of solid (A) from ethanol–ethyl acetate gave fine needles (0·95 g.) of one stereoisomeric form (XVIII*a*) of trans-anti-$\Delta^{9(14)}$-*dodecahydro*-1 : 4-*dihydroxyphenanthrene*, m. p. 217—218° (Found, in a specimen dried at 100° in a high vacuum : C, 75·9; H, 9·9. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

The residue (B), together with the material recovered from the mother-liquors of the preceding crystallisation (total, 0·87 g.), was chromatographed in benzene on alumina (30 g.; Savory & Moore Ltd., deactivated by the addition of 6% of water). Elution with increasing strengths of chloroform in benzene gave, in the following order : (i) an unsaturated diol (80 mg.), m. p. 214—216° after crystallisation from ethyl acetate, identical with (XVIII*a*) (above); (ii) a stereoisomeric unsaturated *diol* (XVIII*b*) (80 mg.), m. p. 194—195° after crystallisation from ethyl acetate (Found : C, 75·6; H, 10·3%); (iii) a third stereoisomeric unsaturated *diol* (XVIII*c*) (150 mg.), m. p. 187—188° [depressed on admixture with (XVIII*b*)] after crystallisation from ethyl acetate (Found : C, 75·5; H, 10·0%).

trans-anti-trans-*Perhydro*-1 : 4-*dioxophenanthrene* (*Diketone E*) (XXIII) *and* trans-anti-trans-*Perhydro*-4-*hydroxy*-1-*oxophenanthrene* (XXII).—*trans-anti*-$\Delta^{9(14)}$-Dodecahydro-1 : 4-dioxophenanthrene (XXI) (7 g.), suspended in methanol (150 c.c.), was hydrogenated at atmospheric pressure and room temperature in presence of palladised strontium carbonate (2 g.). After approximately one mol. of hydrogen had been absorbed (4·5 hr.) the rate of uptake fell. Adams's platinum oxide (100 mg.) was then added and hydrogenation was continued as before, a further molecular proportion being absorbed in the next 4 hr. After removal of the catalyst and solvent, the solid residue was crystallised from ethyl acetate–light petroleum, giving woolly needles (2·45 g.) of trans-anti-trans-*perhydro*-4-*hydroxy*-1-*oxophenanthrene* (XXII), m. p. 138—140° (Found : C, 75·8; H, 10·0. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%). The *acetate*, obtained by the action of acetic anhydride–pyridine at room temperature or by heating with glacial acetic acid containing 1% of toluene-*p*-sulphonic acid, separated from aqueous methanol in colourless needles, m. p. 106—108° (Found : C, 72·4; H, 9·2. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%). The *toluene*-p-*sulphonate*, obtained by the action of toluene-*p*-sulphonyl chloride in dry pyridine, separated from aqueous methanol in needles, m. p. 142—143°, depressed on admixture with the starting material (Found : C, 66·7; H, 7·6. $C_{21}H_{28}O_4S$ requires C, 67·0; H, 7·5%).

The mother-liquors from the crystallisation of (XXII) were evaporated to dryness and the residue, dissolved in acetic acid (100 c.c.), was oxidised with chromium trioxide (3·0 g.). The product, recovered by addition of benzene and water and evaporation of the organic phase, was crystallised from light petroleum, giving fine needles (2 g.) of trans-anti-trans-*perhydro*-1 : 4-*dioxophenanthrene* (diketone E) (XXIII), m. p. 112—113° (Found : C, 76·3; H, 9·0. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%).

Attempts to interrupt the hydrogenation after one mol. of hydrogen had been absorbed gave mixtures from which pure products could not readily be separated, while the use of a palladium catalyst alone made hydrogenation unduly slow during the second stage.

Both diketone E (XXIII) and the hydroxy-ketone (XXII) were stable to treatment with alkaline alumina, and the latter was recovered unchanged after 2 hours' refluxing with 10% methanolic potassium hydroxide, after standing or refluxing with ethanolic sodium ethoxide, and after 15 minutes' refluxing with a solution of potassium *tert.*-butoxide in *tert.*-butanol. Diketone E (XXIII), which was, of course, not stable under these vigorous alkaline conditions, could be dissolved in cold concentrated sulphuric acid and largely recovered by rapid reprecipitation with water.

Interconversion of trans-anti-trans-*Perhydro*-1 : 4-*dioxophenanthrene* (XXIII) *and* trans-anti-trans-*Perhydro*-4-*hydroxy*-1-*oxophenanthrene* (XXII).—(*a*) *trans-anti-trans*-Perhydro-1 : 4-dioxophenanthrene (200 mg.) was shaken in methanol (20 c.c.) under hydrogen in the presence of Adams's platinum oxide (50 mg.) until absorption ceased (*ca.* 30 min.). Removal of the catalyst and evaporation of the solvent gave a solid, yielding on crystallisation from benzene–light petroleum fine needles (170 mg.), m. p. 140—141°, identical with other specimens of the hydroxy-ketone (XXII).

(*b*) *trans-anti-trans*-Perhydro-4-hydroxy-1-oxophenanthrene (50 mg.) in acetic acid (5 c.c.) was oxidised with chromium trioxide (30 mg., 2 equivs.) at room temperature overnight. Isolation in the usual way, using water and chloroform, gave a solid in almost quantitative yield, and recrystallisation from light petroleum afforded flat needles, m. p. 111—112°, identical with other specimens of the diketone (XXIII).

Conversion of trans-anti-trans-*Perhydro*-4-*hydroxy*-1-*oxophenanthrene* (XXII) *into* 1-*Methylphenanthrene*.—*trans-anti-trans*-Perhydro-4-hydroxy-1-oxophenanthrene (2 g.) in benzene (100 c.c.) was added dropwise to a refluxing solution of methylmagnesium iodide (from 2·5 g. of magnesium) in benzene (100 c.c.), and the mixture was heated under reflux for 3·5 hr. After cooling and decomposition of the mixture with excess of dilute sulphuric acid, the product, which was rather insoluble, was isolated by the addition of chloroform and evaporation of the organic phase. Crystallisation of the residue from ethyl acetate afforded fine needles (1·67 g.) of trans-anti-trans-*perhydro*-1 : 4-*dihydroxy*-1-*methylphenanthrene*, m. p. 179—181° (Found, in a specimen dried at 100°/0·1 mm. for 2 hr.: C, 75·6; H, 11.0. $C_{15}H_{26}O_2$ requires C, 75·6; H, 11·0%). The substance (1·5 g.) was dehydrated and dehydrogenated (in the manner described above for *trans-syn-cis*-perhydro-1 : 4-dihydroxy-4-methylphenanthrene) to give 1-methylphenanthrene (0·6 g.), m. p. 119—120° (styphnate, m. p. 149—150°), identical with specimens prepared by alternative routes.

Catalytic Hydrogenation of trans-anti-$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*dihydroxyphenanthrene* (XVIII*a*). trans-anti-trans-*Perhydro*-1 : 4-*dihydroxyphenanthrene* (XXIV*a*).—A solution of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dihydroxyphenanthrene (XVIII*a*) (300 mg.) in methanol (30 c.c.) was shaken in hydrogen in presence of freshly reduced 2% palladium–strontium carbonate (500 mg.). After 71 hr. the catalyst was removed and evaporation of the solvent gave a solid residue. Three recrystallisations from ethyl acetate gave rosettes of needles of trans-anti-trans-*perhydro*-1 : 4-*dihydroxyphenanthrene* (XXIV*a*), m. p. (micro) 190—191° (Found: C, 74·9; H, 10·6. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%); the m. p. was depressed on admixture with a stereoisomeric *trans-anti-trans*-perhydro-1 : 4-dihydroxyphenanthrene (XXIV*b*), m. p. (micro) 194—195°. Oxidation of (XXIV*a*) (130 mg.) in acetic acid (10 c.c.) with chromium trioxide (140 mg.) gave *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (diketone E) (XXIII), m. p. 110—112°, not depressed on admixture with a specimen prepared as described above.

trans-anti-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (*Diketone D*) (XIII), trans-anti-cis-*Perhydro*-1 : 4-*dihydroxyphenanthrenes* (XIX*a*, *b*, *c*), *and* trans-anti-trans-*Perhydro*-1 : 4-*dihydroxyphenanthrene* (XXIV*b*).—(*a*) *trans-anti*-$\Delta^{9(14)}$-Dodecahydro-1 : 4-dioxophenanthrene (XXI) (2 g.) in glacial acetic acid (50 c.c.) was hydrogenated in presence of Adams's platinum oxide (100 mg.) at room temperature and atmospheric pressure until slightly more than three mols. of hydrogen had been absorbed. After removal of the catalyst, chromium trioxide (2·5 g.) in water (10 c.c.) was added and the mixture was set aside overnight. Isolation of the product with the aid of benzene and crystallisation from light petroleum gave fine needles (0·72 g.) of trans-anti-cis-*perhydro*-1 : 4-*dioxophenanthrene* (diketone D) (XIII), m. p. 108—109°, depressed on admixture with the stereoisomeric diketones (diketones A, B, and E) of similar m. p. (Found: C, 76·5; H, 9·2. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%). In one experiment a small quantity of *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (diketone E) (XXIII) was isolated by fractional crystallisation of material remaining in the mother liquors.

(*b*) The mixture of diols resulting from the reduction, as in (*a*), of *trans-anti*-$\Delta^{9(14)}$-dodecahydro-1 : 4-dioxophenanthrene (XXI) (2 g.) was chromatographed on partly deactivated alumina (100 g., Savory & Moore Ltd.; deactivated by addition of 6% of water) in benzene chloroform (9 : 1). Careful elution with increasing concentrations of chloroform in benzene gave four distinct saturated diols. Repeated chromatography of the combined intermediate fractions and mother-liquors gave further quantities of the same substances. The products, listed in the order of elution, were related to *trans-anti-cis*- (diketone D) (XIII) and *trans-anti-trans*-perhydro-1 : 4-dioxophenanthrene (diketone E) (XXIII) by oxidation with chromium trioxide in acetic acid in the usual way. A total yield of 67% of pure saturated diols (all crystallised from ethyl acetate) was obtained: (i) trans-anti-cis-*perhydro*-1 : 4-*dihydroxyphenanthrene* (XIX*a*) (2%), clusters of needles, m. p. (micro) 184—185° (Found: C, 75·0; H, 10·8. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%); oxidation gave diketone D: (ii) trans-anti-cis-*perhydro*-1 : 4-*dihydroxyphenanthrene* (XIX*b*) (13%), fine needles, m. p. (micro) 211° (Found: C, 74·9; H, 11·0%); oxidation gave diketone D: (iii) trans-anti-trans-*perhydro*-1 : 4-*dihydroxyphenanthrene* (XXIV*b*) (18%), woolly needles, m. p. (micro) 194—195° (Found: C, 74·9; H, 10·8%); oxidation gave diketone E: (iv) trans-anti-cis-*perhydro*-1 : 4-*dihydroxyphenanthrene* (XIX*c*) (34%), plates, m. p. (micro) 201° (Found: C, 74·8; H, 11·0%); oxidation gave diketone D.

Reduction of trans-anti-cis-*Perhydro*-1 : 4-*dioxophenanthrene* (*Diketone D*) (XIII) *to* trans-anti-cis-*Perhydro*-1(?)-*hydroxy*-4(?)-*oxophenanthrene* (XX*b*).—*trans-anti-cis*-Perhydro-1 : 4-dioxophenanthrene (400 mg.) in methanol (20 c.c.) was hydrogenated at room temperature and pressure in the presence of Adams's platinum oxide (50 mg.). Uptake of hydrogen ceased after

the absorption of rather more than one mol. in 15 min. On removal of the catalyst and solvent the residue crystallised from benzene–light petroleum giving clusters of needles (330 mg.) of trans-anti-cis-*perhydro*-1(?)-*hydroxy*-4(?)-*oxophenanthrene* (XX*b*), m. p. 144—145° (Found: C, 75·9; H, 10·2. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%). Oxidation of this hydroxy-ketone with chromium trioxide in acetic acid regenerated diketone D. The substance was recovered unchanged after 2·5 hours' heating with 10% alcoholic potassium hydroxide.

Oxidation of cis-syn-cis-*Perhydro*-1 : 4-*dihydroxyphenanthrene* (VIII) *with the Chromium Trioxide–Pyridine Reagent.* cis-syn-cis-*Perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XXIX).—*cis-syn-cis*-Perhydro-1 : 4-dihydroxyphenanthrene (1·0 g.) in pyridine (15 c.c.) was oxidised with the chromium trioxide–pyridine reagent (from 1·5 g. of chromium trioxide, 4·5 equivs.) in pyridine (15 c.c.) at room temperature for 4 hr. The mixture was then poured into water and extracted five times with chloroform, frequent filtration being necessary to remove the flocculent brown matter that separated. The combined chloroform extracts were washed free from pyridine with dilute sulphuric acid, then with water and dilute sodium hydrogen carbonate, dried, and evaporated. The resulting viscous brown oil was extracted several times with boiling light petroleum, and a small brown residue was discarded. On cooling, the combined almost colourless extracts deposited a mixture of small dense prisms and flocculent woolly needles, and these were hand-sorted. The woolly needles had an indeterminate m. p., not improved by recrystallisation, and they were combined with material recovered from the mother-liquors for subsequent chromatography. The prisms, on recrystallisation from ethyl acetate–light petroleum, afforded cis-syn-cis-*perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XXIX) in the form of rods (150 mg.), m. p. 123—124° (Found: C, 75·9; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

The uncharacterised material (0·77 g.) was dissolved in benzene–light petroleum (1 : 1) and chromatographed on a column of alkaline alumina (30 g., Peter Spence & Sons, Ltd., type H), and elution with benzene and benzene containing a progressively increasing proportion of chloroform gave first a diketone fraction and then a hydroxy-ketone fraction.

The diketone fraction (120 mg.), on crystallisation from light petroleum, gave a mixture of two crystal forms, which, on repeated hand-sorting and recrystallisation, afforded *trans-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone B) (V), m. p. 115—116°, and *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone C) (XII), m. p. 141°, identical with specimens obtained previously. These were presumably derived from the alkaline rearrangement of *cis-syn-cis*-perhydro-1 : 4-dioxophenanthrene (diketone A) (III), present originally in the oxidation product.

The hydroxy-ketone fraction (350 mg.), on crystallisation from ethyl acetate–light petroleum, afforded *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*a*) (130 mg.) in the form of rectangular plates, m. p. 172—173°, identical with specimens obtained by an alternative route; this substance was obviously derived from the *cis-syn-cis*-compound (XXIX), partly isolated above by direct crystallisation from the reaction product (see following experiment). The mother-liquors on concentration deposited rosettes of fine needles, m. p. *ca.* 125—130°, which could not be further purified by repeated crystallisation, but the m. p. was raised on admixture with *trans-syn-cis*-perhydro-4-hydroxy-1-oxophenanthrene (VI), m. p. 141°; out of seventeen prominent bands in the 900—1300 cm.$^{-1}$ region of the infra-red absorption spectrum of the material, m. p. *ca.* 125—130°, fifteen were also found in that of (VI) and three in that of (XX*a*). *trans-syn-cis*-Perhydro-4-hydroxy-1-oxophenanthrene (VI), if present, could have been derived from a *cis-syn-cis*-precursor (IV), present in the original oxidation product, on passage over alkaline alumina.

Stereoisomerisation of cis-syn-cis-*Perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XXIX). trans-anti-cis-*Perhydro*-1-*hydroxy*-4-*oxophenanthrene* (XX*a*).—A solution of *cis-syn-cis*-perhydro-1-hydroxy-4-oxophenanthrene (50 mg.) in methanolic potassium hydroxide (10 c.c. of 5%) was heated under reflux for 1 hr. After partial removal of solvent by distillation, addition of water gave an almost quantitative yield of *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*a*) in the form of lustrous plates, m. p. 171—172°, not depressed on admixture with specimens obtained by other routes.

Oppenauer Oxidation of cis-syn-cis-*Perhydro*-1 : 4-*dihydroxyphenanthrene* (VIII).—A solution of *cis-syn-cis*-perhydro-1 : 4-dihydroxyphenanthrene (0·9 g.) in benzene (50 c.c.) containing *cyclo*hexanone (10 c.c.) was heated under reflux with aluminium *iso*propoxide (1·0 g.) for 7 hr. After cooling, water (2 c.c.) was added and the precipitated alumina was collected. The filtrate was evaporated under reduced pressure, finally at 100°/1 mm., and the residual oil was taken up in hot light petroleum. A small quantity of crystalline material separated on pro-

longed standing, but this had an indefinite m. p., and could not be further purified on recrystallisation. The entire reaction product (0·83 g.) was then chromatographed in benzene–light petroleum (1 : 1) on alkaline alumina (30 g., Peter Spence & Sons, Ltd., type H). Elution with benzene containing a progressively increasing proportion of chloroform afforded a diketone fraction followed by a hydroxy-ketone fraction.

The diketone fraction (230 mg.) was shown to be a mixture of *trans-syn-cis-* (diketone B) (V) and *cis-anti-cis*-perhydro-1 : 4-dioxophenanthrene (diketone C) (XII), by crystallisation and hand-sorting as described above.

The hydroxy-ketone fraction (250 mg.), on recrystallisation, afforded rectangular plates (200 mg.) of *trans-anti-cis*-perhydro-1-hydroxy-4-oxophenanthrene (XX*a*), m. p. 172—173°, not depressed on admixture with specimens obtained by other routes. No further crystalline material could be obtained from the mother-liquors.

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