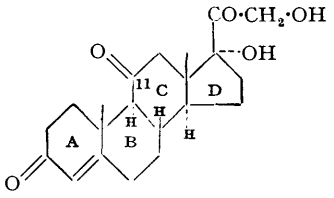
117. *Studies of the Diels–Alder Reaction. Part I. The Reaction between* 1-*Vinyl*cyclo*hex*-1-*ene and Benzoquinone, and the Reduction of* $\Delta^{2:9(14)}$-*Decahydro*-1 : 4-*diketophenanthrene.*

By P. A. Robins and James Walker.

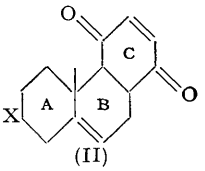
The Diels–Alder reaction between 1-vinyl*cyclo*hex-1-ene and benzoquinone afforded the highly characteristic $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (V), and the reduction of (V) under a variety of conditions has been studied. Reduction with zinc and acetic acid under mild conditions gave $\Delta^{9(14)}$-dodecahydro-1 : 4-diketophenanthrene (VIII), and catalytic hydrogenation under progressively vigorous conditions gave perhydro-1 : 4-diketophenanthrene (XII), perhydro-4-hydroxy-1-ketophenanthrene (XIII), and perhydro-1 : 4-dihydroxyphenanthrene (XVI). These reactions are discussed in the light of the stereochemical factors involved.

Methods for the construction of the tetracyclic steroid nucleus from hydro-1-ketophenanthrene derivatives are now well known and their application to hydro-1-ketophenanthrenes suitably substituted in the 4-position could be made the basis for the synthesis of cortisone (I) and similar compounds having a substituent in the 11-position (steroid enumeration). Such compounds are to be found in the decahydro-1 : 4-diketophenanthrenes (II), which should be available as the products of Diels–Alder reactions between suitably substituted vinyl*cyclo*hexenes (III) and benzoquinone, and the stereochemical problems involved are not such as might prove to be insuperable. The stereochemistry of the sterol system is now well understood and the predictable stereochemical course of the Diels–Alder reaction enables one to assign configurations to adducts, such as (II), with some degree of confidence. Furthermore, the presence of carbonyl groups adjacent to asymmetric centres permits selective inversions to be effected at appropriate stages in order to relate the configurations of the synthetic materials to those of the natural products.

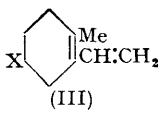
We have commenced a study of this problem by undertaking an examination of the Diels–Alder reaction between vinyl*cyclo*hexene and benzoquinone, together with an examination of the controlled reduction of the resulting product. The reaction between



(I)



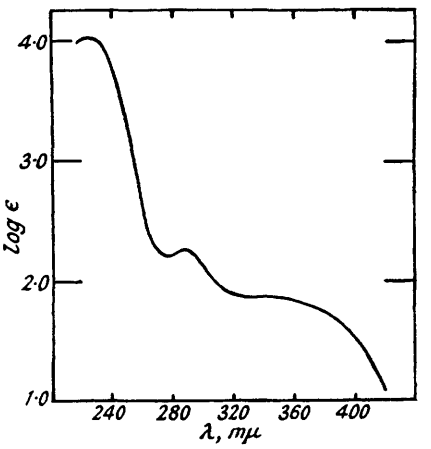
(II)



(III)

vinyl*cyclo*hexene and benzoquinone, to give $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (IV), has been recorded by Cook and Lawrence (*J.*, 1938, 58) and by Backer and van der Bij (*Rec. Trav. chim.*, 1943, **62**, 561), and Grob, Jundt, and Wicki (*Helv. Chim. Acta*, 1949, **32**, 2427) used this substance (IV) to gain access to 1 : 4-dimethoxyphenanthrene. No stereochemical considerations have, however, been mentioned nor has any study of the reduction of (IV) been carried out hitherto. It has been found extremely difficult to obtain really pure specimens of 1-vinyl*cyclo*hexene, and the use of greater amounts than *ca.* 0·6 molecular proportion of benzoquinone in the Diels–Alder reaction has resulted in the presence of unchanged quinone in the product. The difficulties are doubtless attributable to lack of marked discontinuity in the rate of hydrogenation of 1-ethynyl*cyclo*hexanol, with the result that the intermediate 1-vinyl*cyclo*hexanol may be contaminated with some 1-ethyl*cyclo*hexanol, and to the possibility of unchanged 1-vinyl*cyclo*hexanol co-distilling with the hydrocarbon in the subsequent preparation of 1-vinyl*cyclo*hexene. The product (IV), however, is an extremely characteristic substance, although it is notable for its extreme lability in the presence of traces of alkali. The light absorption of (IV) (Fig. 1), containing the interesting –CO·CH:CH·CO– chromophore, appeared to be intermediate between that of the quinone adduct of lævopimaric acid and that of diacetylethylene as recorded by Ruzicka and Kaufmann (*Helv. Chim. Acta*, 1941, **24**, 1425).

FIG. 1.

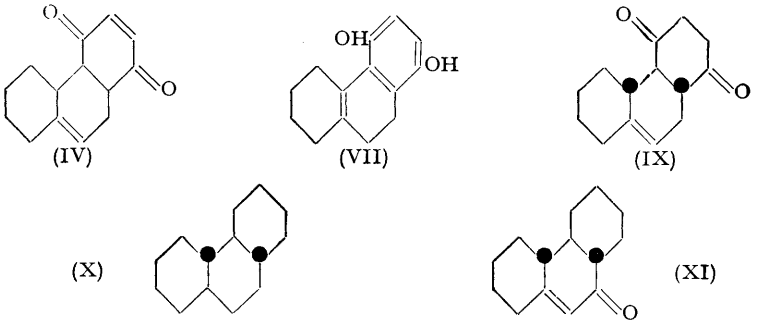


$\Delta^{2:9(14)}$-*Decahydro*-1 : 4-*diketophenanthrene* (IV).

From the so-called Alder rules (Alder and Stein, *Angew. Chem.*, 1937, **50**, 510; cf. Bergmann and Eschinazi, *J. Amer. Chem. Soc.*, 1943, **65**, 1405) one can assign to (IV) the *syn-cis*-configuration (V) (see p. 645), in which the dots indicate that hydrogen atoms so denoted are on the side of the carbon skeleton nearer to the reader (cf. Linstead, *Chem. and Ind.*, 1937, **56**, 510; Linstead and Walpole, *J.*, 1939, 842). The substance (V) was readily aromatised to 5 : 6 : 7 : 8 : 10 : 13-hexahydro-1 : 4-dihydroxyphenanthrene (VI) by treatment either with alkali or with acid (cf. Grob *et al.*, *loc. cit.*), and the close correspondence between the light absorption of (VI) and that of quinol (Fig. 2) indicates that the remaining isolated double bond had not moved into the 13 : 14-position into conjugation with the aromatic ring to give (VII).

Treatment of (V) with zinc powder and acetic acid at room temperature effected reduction at the 2 : 3-double bond to give $\Delta^{9(14)}$-dodecahydro-1 : 4-diketophenanthrene in excellent yield, and there is no reason to believe, considering the mildness of the conditions used, that this substance is other than the *syn-cis*-compound (VIII). On the other hand, reduction with zinc in hot acetic acid gave either a stereoisomeric $\Delta^{9(14)}$-dodecahydro-1 : 4-diketophenanthrene, in which inversion at either $C_{(11)}$ or at $C_{(12)}$ had taken place,

or the isomeric Δ^{13}-dodecahydrodiketophenanthrene. In the event of this substance's being a stereoisomeride of (VIII), it is unlikely that inversion at both $C_{(11)}$ and $C_{(12)}$ would have taken place to give the *anti-cis*-compound, with *cis*-fusion of rings B and C, but it is distinctly probable that equilibration of (VIII) would give the *anti-trans*-compound



(IX), in line with the greatest stability of the *trans-anti-trans*-form (X) among perhydrophenanthrenes (cf. Johnson, *Experientia*, 1951, **8**, 315), and the fact that the addition product of sodio*cyclo*hexanone to acetyl*cyclo*hexene is the *anti-trans*-compound (XI) (Linstead, Davis, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 2009). Further reduction of (VIII) by catalytic hydrogenation in the presence of palladised strontium carbonate

FIG. 2. FIG. 3.

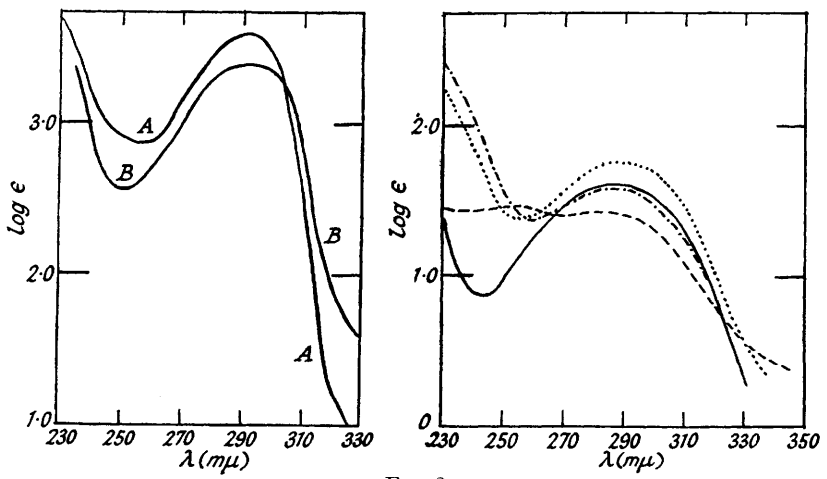


FIG. 2.

A 5 : 6 : 7 : 8 : 10 : 13-*Hexahydro*-1 : 4-*dihydroxyphenanthrene* (VI).
B *Quinol.*

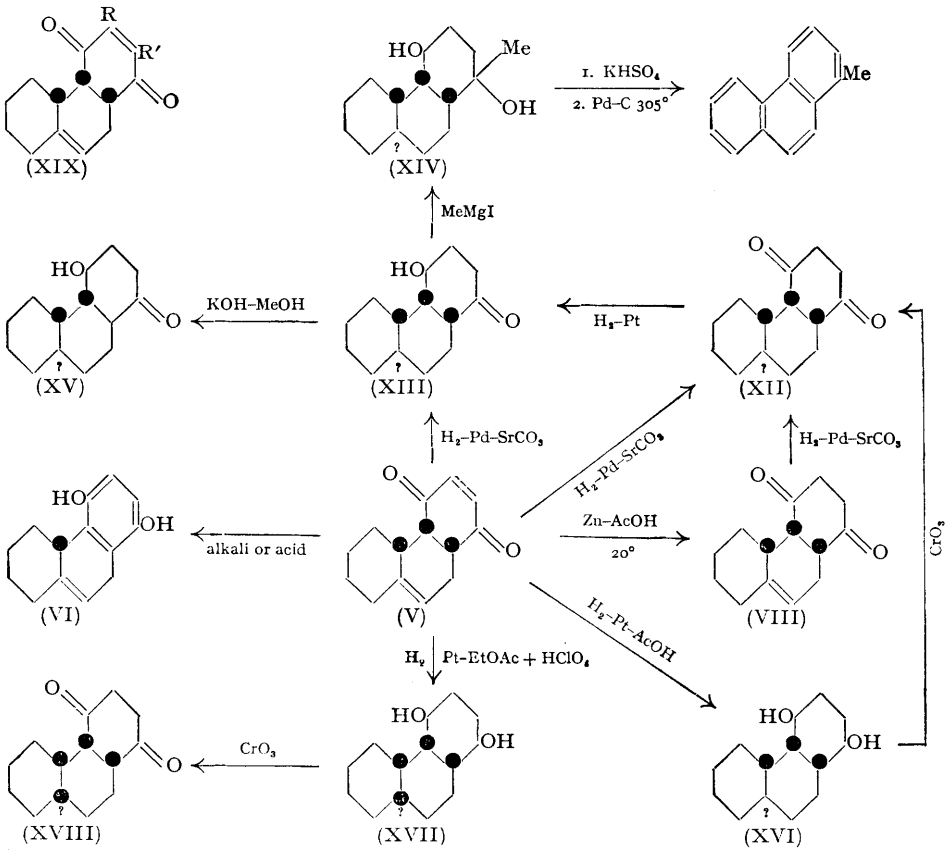
FIG. 3.

— · — · — · — $\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*diketophenanthrene* (VIII).
———— *Perhydro*-1 : 4-*diketophenanthrene* (XII).
– – – – – – – – *Perhydro*-4-*hydroxy*-1-*ketophenanthrene* (XIII).
. . . . . *Compound* (IX).

afforded perhydro-1 : 4-diketophenanthrene (XII), and the same compound was obtainable by direct hydrogenation of (V). In (XII) the stereochemical configuration at $C_{(14)}$ is not readily predictable, but provisionally (XII) may be assigned the *trans-syn-cis*-configuration, by analogy with the hydrogenation of (XI) to the *trans-anti-trans*-perhydro-9-ketophenanthrene (Linstead *et al.*, *loc. cit.*). This provisional assignment of the configuration of (XII) would imply that ring C does not interfere with the hydrogenation of the 9(14)-double bond in (VIII) to any appreciable extent by catalyst hindrance (cf. Linstead *et al.*, *ibid.*, p. 1985). In addition to being produced in hydrogenations with a palladium

catalyst in neutral solution, (XII) was also obtained from diol A (see below), obtained by complete hydrogenation of (V) with Adams's platinum oxide catalyst in acidic media, indicating the same stereochemical course for the hydrogenation of the 9(14)-double bond under both sets of conditions. Light-absorption data for these ketonic compounds are collected in Fig. 3.

Further hydrogenation of (XII) with Adams's platinum oxide catalyst afforded a keto-alcohol (XIII), and the same compound, surprisingly, was also obtained from (V) directly by prolonged hydrogenation in the presence of palladised strontium carbonate. The constitution of (XIII) followed from the fact that treatment with methylmagnesium iodide, dehydration of the resulting perhydro-1 : 4-dihydroxy-1-methylphenanthrene (XIV), and dehydrogenation with palladised charcoal afforded 1-methylphenanthrene. The *cis*-configuration of (XIII) at the B–C ring fusion followed from the fact that, being a derivative of *cis*-α-decalone, it was readily converted into a stereoisomeride (XV) by treatment with 1% methanolic alkali. Exhaustive hydrogenation of (V) in the presence of Adams's catalyst in acetic acid solution gave a perhydro-1 : 4-dihydroxyphenanthrene (diol A), which was isolated by way of its dibenzoate and subsequent hydrolysis. The yields of the dibenzoate were variable but the rate of hydrogenation was greatly accelerated by the addition of a small proportion of perchloric acid (cf. Hershberg *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 1144). On oxidation with chromic acid, this diol (diol A) afforded



the perhydro-1 : 4-diketophenanthrene (XII), which we had already obtained directly from (V) and also from (VIII); diol A is therefore assigned configuration (XVI). In ethyl acetate containing a small proportion of perchloric acid, however, hydrogenation of (V) afforded, in addition to (XVI), a second crystalline perhydro-1 : 4-dihydroxyphenanthrene (diol B), giving rise on oxidation with chromic acid to a perhydro-1 : 4-diketo-

phenanthrene stereoisomeric with (XII); the stereochemical differences between diol A and diol B and the two derived ketones are probably associated with $C_{(14)}$, rather than with $C_{(11)}$ or $C_{(12)}$, and diol B is therefore provisionally assigned configuration (XVII) and the derived diketone is assigned configuration (XVIII).

The Diels–Alder reaction between 1-vinyl*cyclo*hex-1-ene and toluquinone gave a mixture of products (XIX; R = H, R′ = Me) and (XIX; R = Me, R′ = H) which could only be separated with difficulty.

Experimental

1-*Ethynyl*cyclo*hexanol*.—Redistilled *cyclo*hexanone (196 g., 2·0 g.-mol.) in dry ether (400 c.c.) was added during 45 minutes to a stirred suspension of sodium acetylide [prepared from 92 g. of sodium (4 g.-atoms) by the method of Heilbron, Jones, and Weedon (*J.*, 1945, 83)] in liquid ammonia (*ca.* 3·5 l.), contained in a large Dewar vessel, through which a slow stream of gaseous acetylene was being passed. After 7 hours' stirring the mixture was kept overnight. Ammonium chloride (216 g., 4 g.-mol.) was then added in small portions with stirring, and the greater part of the ammonia allowed to evaporate. Much water was then added to the semi-solid mass, and the organic layer was separated. The aqueous layer was saturated with sodium chloride and extracted three times with ether. The combined organic layers were washed with 2N-sulphuric acid until free from ammonia, dried (Na_2SO_4), and fractionated twice, giving ethynyl*cyclo*hexanol (186 g.), b. p. 74—78°/18 mm., n_D^{20} 1·4859; a small fore-run containing a trace of *cyclo*hexanone was rejected in each distillation. The product slowly solidified to a low-melting solid. *Inter alios*, Campbell *et al.* (*J. Amer. Chem. Soc.*, 1938, **60**, 2882) record b. p. 74°/14 mm., n_D^{20} 1·4820; Chanley (*ibid.*, 1948, **70**, 244) records m. p. 28—30°.

1-*Vinyl*cyclo*hexanol*.—(a) *By catalytic hydrogenation.* 1-Ethynyl*cyclo*hexanol (62 g., 0·5 g.-mol.) in methanol (200 c.c.) was stirred with 2% palladised strontium carbonate (6 g.) in an atmosphere of hydrogen until the calculated volume required for semihydrogenation of the ethynyl group had been absorbed. After removal of the solvent from the filtered solution through a short Dufton column, the residue was distilled under reduced pressure, to give 1-vinyl*cyclo*hexanol (50 g.), b. p. 66—68°/14 mm., n_D^{20} 1·4798. Nazarov *et al.* (*Bull. Acad. Sci. U.S.S.R.*, 1946, 305; *Chem. Abs.*, 1949, **43**, 6969) record b. p. 67·5—68°/15 mm., n_D^{20} 1·4740.

(b) *By reduction with sodium and ethanol in liquid ammonia* (cf. Birch, *J.*, 1945, 809). Sodium (25·5 g.) was added in small portions with vigorous stirring to a solution of 1-ethynyl*cyclo*hexanol (62 g., 0·5 g.-mol.) in liquid ammonia (*ca.* 500 c.c.) containing ethanol (51 g.). After most of the ammonia had been allowed to evaporate, water (250 c.c.) was added and the product was recovered in ether. Fractionation afforded 1-vinyl*cyclo*hexanol (27·6 g.), b. p. 76°/17 mm.

1-*Vinyl*cyclo*hex*-1-*ene*.—1-Vinyl*cyclo*hexanol (61 g.) was slowly distilled in a stream of nitrogen from a flask containing powdered potassium hydrogen sulphate (5 g.) and heated at 150° (oil-bath). The distillate, after separation from the aqueous layer and drying (K_2CO_3), was redistilled in a stream of nitrogen from potassium hydrogen sulphate (1 g.), to give 1-vinyl-*cyclo*hex-1-ene (46·1 g.), b. p. 143—144°, n_D^{19} 1·4950. Nazarov and Nagibina (*J. Gen. Chem. U.S.S.R.*, 1948, **18**, 1090; *Chem. Abs.*, 1949, **43**, 1333) record b. p. 142—144°, n_D^{19} 1·4915.

Benzoquinone.—Benzoquinone was prepared from quinol (*Org. Synth.*, **16**, 73) and purified by steam-distillation before use.

$\Delta^{2:9(14)}$-*Decahydro*-1 : 4-*diketophenanthrene* (V).—Benzoquinone (6 g., 0·6 mol.) was added in small portions during 30 minutes to a stirred solution of 1-vinyl*cyclo*hex-1-ene (10 g.) in methanol (50 c.c.), each portion being allowed to dissolve before another was added. After a further 30 minutes' stirring, the reaction mixture was left at room temperature for 4 hours, during which a crystalline solid began to separate; it was then diluted with water (5 c.c.) and cooled to −5°. Filtration afforded massive pale yellow prisms of $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (V) (10·7 g., 88% on benzoquinone), m. p. 85—87°. An analytical sample crystallised from light petroleum had m. p. 87—88°; light absorption in ethanol, $\lambda_{max.}$ 225, 290, 340 mμ, log $\varepsilon_{max.}$ 4·08, 2·15, 1·90 (Found: C, 77·7; H, 7·3. Calc. for $C_{14}H_{16}O_2$: C, 77·7; H, 7·5%). Cook and Lawrence (*J.*, 1938, 58) record m. p. 84—84·5° for their product which was crystallised from methanol: this observation was confirmed by Backer and van der Bij (*Rec. Trav. chim.*, 1943, **62**, 571), who also state that crystallisation from light petroleum gave needles, m. p. 136—137°. Although we have used light petroleum exclusively as a solvent we have not encountered material of this higher m. p.

The compound was very sensitive to alkali, and decomposed slowly if stored in a soda-glass container; it was best stored in the dark in a Pyrex flask. The use of a full molecular

proportion of benzoquinone did not improve the yield and caused difficulty by crystallisation of the quinone from the reaction mixture with the product. Variation in the method of preparation of the 1-vinyl*cyclo*hexanol (see above) did not affect the final yield of decahydrodiketophenanthrene from 1-vinyl*cyclo*hex-1-ene.

5 : 6 : 7 : 8 : 10 : 13-*Hexahydro*-1 : 4-*dihydroxyphenanthrene* (VI).—(*a*) A solution of $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (200 mg.) in methanol (50 c.c.) was treated with 2N-aqueous sodium hydroxide (3 c.c.). After the reactants had been mixed by swirling, during which a darkening in colour took place, 2N-hydrochloric acid (10 c.c.) was added, and the mixture was diluted with water and extracted with ether. The ethereal extract, after being washed with water and dried (Na_2SO_4), afforded, on evaporation, 5 : 6 : 7 : 8 : 10 : 13-hexahydro-1 : 4-dihydroxyphenanthrene (VI) (150 mg.), which separated from benzene–light petroleum in stout needles, m. p. 175—177°; light absorption in ethanol, $\lambda_{max.}$ 292 mμ, log $\varepsilon_{max.}$ 3·6. Grob *et al.* (*Helv. Chim. Acta*, 1949, **32**, 2427) record m. p. 175—177°. The substance was soluble in aqueous alkali, giving a solution that darkened rapidly in air.

(*b*) A solution of the decahydrodiketophenanthrene (V) (200 mg.) in methanol (10 c.c.) was boiled under reflux with concentrated hydrochloric acid (0·5 c.c.). The product was isolated by cooling, dilution with water, and extraction with ether. Crystallisation from benzene–light petroleum gave a product (VI) identical with that obtained in (*a*).

$\Delta^{9(14)}$-*Dodecahydro*-1 : 4-*diketophenanthrene* (VIII).—$\Delta^{2:9(14)}$-Decahydro-1 : 4-diketophenanthrene (1 g.) was dissolved in glacial acetic acid (50 c.c.), and zinc powder (1 g.) was added to the stirred solution at room temperature. After 5 minutes' stirring the unchanged zinc was filtered off and washed with a little ether, and the combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was extracted with boiling light petroleum, which, after filtration and cooling, deposited clusters of small, colourless prisms (0·84 g.) of $\Delta^{9(14)}$-*dodecahydro*-1 : 4-*diketophenanthrene* (VIII), m. p. 81—82; light absorption in ethanol, $\lambda_{max.}$ 286 mμ, log $\varepsilon_{max.}$ 1·58 (Found: C, 77·0; H, 8·6. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). The *bis*-2 : 4-*dinitrophenylhydrazone* separated from methanol–ethyl acetate as an amorphous yellow powder, which sintered and decomposed above 145° (Found: N, 19·3. $C_{26}H_{26}O_8N_8$ requires N, 19·4%).

Reduction of $\Delta^{2:9(14)}$-*Decahydro*-1 : 4-*diketophenanthrene* (V) *with Zinc in Boiling Acetic Acid.*—A solution of the diketone (1 g.) in glacial acetic acid (60 c.c.) was boiled under reflux with zinc powder (3·6 g.) for 4 hours. After cooling, zinc acetate and unused zinc were removed by filtration and the filtrate was evaporated under reduced pressure. The residue was extracted with boiling light petroleum and, on cooling, the extract deposited rosettes of fine needles (300 mg.). A further crystallisation from light petroleum gave a *compound* (?IX), m. p. 138—139°, which gave a pale yellow colour with tetranitromethane; light absorption in ethanol, $\lambda_{max.}$ 289 mμ, log $\varepsilon_{max.}$ 1·76 (Found: C, 77·1; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). The *bis*-2 : 4-*dinitrophenylhydrazone* separated from toluene as a yellow amorphous powder, m. p. 242—243° (decomp.) (Found: N, 18·9. $C_{26}H_{26}O_8N_8$ requires N, 19·4%).

Perhydro-1 : 4-*diketophenanthrene* (XII).—(*a*) $\Delta^{2:9(14)}$-Decahydro-1 : 4-diketophenanthrene (V) (5 g.) in methanol (150 c.c.) was shaken with 2% palladised strontium carbonate (2 g.) in hydrogen at room temperature and pressure until 2 molecular proportions of hydrogen had been absorbed (about 3 hours). After filtration and removal of the solvent the residue, crystallised from aqueous methanol, afforded colourless needles (3·05 g.) of perhydro-1 : 4-diketophenanthrene (XII), m. p. 107—109° alone and in admixture with the product obtained by oxidation of diol A (see below). Substitution of a platinum oxide catalyst in this hydrogenation gave a gummy product that could not be crystallised.

(*b*) A solution of $\Delta^{9(14)}$-dodecahydro-1 : 4-diketophenanthrene (VIII) (500 mg.) in ethyl acetate (40 c.c.) was shaken in hydrogen with Adams's platinum oxide catalyst (50 mg.) until 1 molecular proportion of hydrogen had been absorbed. After removal of the catalyst and evaporation of the solvent, crystallisation of the residue from light petroleum gave perhydro-1 : 4-diketophenanthrene (XII) (0·34 g.), m. p. 108—109°, alone and in admixture with specimens obtained by alternative routes.

Perhydro-4-*hydroxy*-1-*ketophenanthrene* (XIII).—(*a*) A solution of $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (V) (500 mg.) in methanol (20 c.c.) was shaken with 2% palladised strontium carbonate (0·5 g.) in hydrogen at room pressure and temperature for 24 hours; 2·6 molecular proportions of hydrogen had then been absorbed and the rate of uptake had become negligible. After removal of the catalyst and evaporation of the solvent, the residue crystallised. Recrystallisation from a large volume of light petroleum or, preferably, ligroin, gave felted needles (350 mg.) of *perhydro*-4-*hydroxy*-1-*ketophenanthrene* (XIII), m. p. 136—138°; light absorption

in ethanol, $\lambda_{max.}$ 254, 282 mμ, log $\varepsilon_{max.}$ 1·46, 1·43 (Found: C, 75·7, 75·8, 75·3; H, 9·8, 9·6, 10·1. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%). The 2 : 4-*dinitrophenylhydrazone* separated from benzene in small orange needles, m. p. 219—221° (Found: N, 14·5. $C_{20}H_{26}O_5N_4$ requires N, 14·0%). The *acetate* crystallised from light petroleum at −5° in flattened needles, m. p. 79—80° (Found: C, 72·5; H, 9·4. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%).

(*b*) A solution of perhydro-1 : 4-diketophenanthrene (XII) (4·0 g.) in methanol (100 c.c.) was shaken in hydrogen at room pressure and temperature with Adams's platinum oxide catalyst (200 mg.) for 4 hours, 0·86 molecular proportion of hydrogen being absorbed. Isolation of the product in the usual way and crystallisation from ligroin (250 c.c.) afforded felted needles (3·0 g.) of perhydro-4-hydroxy-1-ketophenanthrene (XIII), m. p. 138—139° alone and in admixture with the product obtained in (*a*) above.

Perhydro-4-hydroxy-1-ketophenanthrene (XV).—A solution of perhydro-4-hydroxy-1-ketophenanthrene (XIII) (200 mg.) in 1% methanolic potassium hydroxide (20 c.c.) was boiled under reflux for 30 minutes. The product was isolated by dilution with water, and crystallisation from ligroin gave needles (150 mg.) of the stereoisomeric *perhydro-4-hydroxy-1-ketophenanthrene* (XV), m. p. 141—142°, depressed to 105—110° on admixture with the starting material (Found: C, 75·3; H, 9·8. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

Perhydro-1 : 4-dihydroxyphenanthrene.—(*a*) A solution of $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (500 mg.) in glacial acetic acid (30 c.c.) was shaken in hydrogen at room pressure and temperature with Adams's platinum oxide catalyst (50 mg.) until 4 molecular proportions of hydrogen had been absorbed; about 72 hours were required and a fresh portion of catalyst was added after 48 hours. The gum obtained by removal of the catalyst and evaporation of the solvent was treated with benzoyl chloride in pyridine overnight at room temperature. Isolation of the neutral material with ether gave a gum, which, on dissolution in a small volume of methanol, deposited massive prisms of 1 : 4-*dibenzoyloxyperhydrophenanthrene* (diol A dibenzoate) (450 mg., 45%), m. p. 130—134°. A specimen, recrystallised from ethyl acetate, had m. p. 134—135° (Found: C, 77·9; H, 7·4. $C_{28}H_{32}O_4$ requires C, 77·8; H, 7·5%). The rate of hydrogenation could be greatly increased by the addition of a small quantity of 72% perchloric acid (cf. Hershberg *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 1144), but the yields of diol A dibenzoate varied.

Hydrolysis of this dibenzoate by refluxing it with excess of 5% methanolic potassium hydroxide for 30 minutes gave *perhydro-1 : 4-dihydroxyphenanthrene* (XVI) (diol A), which separated from light petroleum containing a little ethyl acetate in prisms, m. p. 134—135°, depressed to 110—115° on admixture with the dibenzoate (above) of the same m. p. (Found: C, 75·0; H, 10·6. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%).

Oxidation of the diol with chromium trioxide (2·2 mols.) in glacial acetic acid at room temperature overnight gave *perhydro-1 : 4-diketophenanthrene* (XII), which separated from light petroleum in clusters of needles, m. p. 108·5—110°; light absorption in ethanol, $\lambda_{max.}$ 285 mμ, log $\varepsilon_{max.}$ 1·62 (Found: C, 76·3; H, 9·5. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%). The *bis*-2 : 4-*dinitrophenylhydrazone* separated from methoxyethanol as a brick-red powder, which sintered and decomposed above 165° (Found: N, 18·9. $C_{26}H_{28}O_8N_8$ requires N, 19·3%).

(*b*) A solution of $\Delta^{2:9(14)}$-decahydro-1 : 4-diketophenanthrene (1·0 g.) in ethyl acetate (100 c.c.), containing perchloric acid (0·1 c.c. of 70%), was shaken in hydrogen at room pressure and temperature with Adams's platinum oxide catalyst (100 mg.) until absorption of hydrogen ceased, four molecular proportions being absorbed in 3½ hours. After removal of the catalyst, the ethyl acetate solution was washed with aqueous sodium hydrogen carbonate to remove perchloric acid and then concentrated (to *ca.* 10 c.c.). Addition of an equal volume of light petroleum gave a white solid (160 mg.), which, on crystallisation from benzene–ethanol, gave fine needles of a stereoisomeric *perhydro-1 : 4-dihydroxyphenanthrene* (XVII) (diol B), m. p. 212° (Found: C, 75·5; H, 10·9. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%). Diol B, on oxidation with chromium trioxide (2·2 mols.) in glacial acetic acid, gave a stereoisomeric *perhydro-1 : 4-diketophenanthrene* (XVIII), crystallising from light petroleum in fine needles, m. p. 115—116°, depressed on admixture with the perhydro-diketone (XII), m. p. 108·5—110°, from diol A (Found: C, 76·6; H, 9·5. $C_{14}H_{20}O_2$ requires C, 76·2; H, 9·1%).

The remainder of the hydrogenation product, after separation of diol B, was isolated by evaporation of the solvent. The resultant gum, after treatment with benzoyl chloride and pyridine in the usual way, followed by recovery of the neutral fraction in ether, afforded the dibenzoate (220 mg.) of diol A.

Perhydro-1 : 4-dihydroxy-1-methylphenanthrene (XIV).—The keto-alcohol (XIII) (2·0 g.) in

dry benzene (60 c.c.) was added to a stirred, boiling solution of methylmagnesium iodide (from 2·5 g. of magnesium and 14·5 g. of methyl iodide) in benzene (100 c.c.). After being stirred under reflux for 3½ hours, the reaction mixture was cooled to 0° and decomposed with ice-cold 4N-sulphuric acid (50 c.c.). After separation of the benzene layer, the aqueous phase was extracted once with ether, and the combined organic layers were washed successively with 2N-sulphuric acid, water, and saturated aqueous sodium hydrogen carbonate. Removal of the solvent left a gum (2·08 g.), which appeared, from its behaviour with Brady's reagent, still to contain a trace of ketonic material. The gum was dissolved in ethanol (90 c.c.) and glacial acetic acid (10 c.c.) and refluxed with Girard's reagent P (5 g.) for 30 minutes. After cooling and pouring into water containing 2N-sodium hydroxide (75 c.c.; 90% of that required for neutralisation of the acetic acid), the non-ketonic fraction was recovered in ether. Evaporation of the dried ethereal solution gave a gum (1·89 g.), which solidified on trituration with light petroleum to give *perhydro*-1 : 4-*dihydroxy*-1-*methylphenanthrene* (1·40 g.), m. p. 115—121°. Crystallisation from light petroleum afforded colourless prisms, m. p. 123°, giving no colour with tetranitromethane (Found: C, 75·4; H, 10·7. $C_{15}H_{26}O_2$ requires C, 75·6; H, 11·0%).

Dehydration and Dehydrogenation of (XIV) *to* 1-*Methylphenanthrene*.—Crude perhydro-1 : 4-dihydroxy-1-methylphenanthrene (1·3 g.) and potassium hydrogen sulphate (2·5 g.) were heated in an atmosphere of nitrogen to 180° for 30 minutes. After cooling and addition of water, the organic material was isolated with ether. The dried ethereal solution was evaporated, and the oily residue, taken up in low-boiling light petroleum, was allowed to run through a short column of activated alumina (Peter Spence & Sons Ltd., Type H). The eluate, on distillation, yielded an oily residue (0·7 g.), giving a deep brown colour with tetranitromethane. The oil was heated at 300—310° (metal-bath) with palladised charcoal (1·0 g., containing 10% of palladium) in diphenylamine under reflux in a slow stream of carbon dioxide. The effluent gases were collected in a graduated receiver over 40% aqueous potassium hydroxide. After 5 hours' heating, no further evolution of hydrogen took place (total vol., 260 c.c.; calc. for a decahydromethylphenanthrene, 390 c.c.). The mixture was cooled, taken up in ether, and filtered, and the filtrate was saturated with dry hydrogen chloride. After filtration of the diphenylamine hydrochloride and washing with ether, the filtrate and washings were evaporated to dryness, giving a brown oil. This residue, dissolved in low-boiling light petroleum, was passed through a short column of activated alumina. Elution with the same solvent and evaporation of the effluent gave a white, crystalline solid (0·6 g.), m. p. 105—112°. Two crystallisations from methanol afforded pure 1-methylphenanthrene, m. p. 120—121° (Found: C, 93·2; H, 6·5. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%). The hydrocarbon formed a picrate, m. p. 134—135°, and a styphnate, m. p. 149—150°. Haworth (*J.*, 1932, 1125) gives 1-methylphenanthrene, m. p. 118°, picrate m. p. 139°, styphnate m. p. 149—150°; Bachmann and Wilds (*J. Amer. Chem. Soc.*, 1938, **60**, 624) give 1-methylphenanthrene m. p. 120—121°, picrate m. p. 136—136·5°.

Addition of 1-*Vinyl*cyclo*hex*-1-*ene to Toluquinone*.—A mixture of 1-vinyl*cyclo*hex-1-ene (5 g.) and toluquinone (5 g.) in benzene (75 c.c.) was heated under reflux for 4 hours. On removal of the solvent under reduced pressure, the residual oil was dissolved in a mixture of methanol (100 c.c.) and water (30 c.c.) and kept at 0° overnight. The resultant crop of fine, pale yellow needles, m. p. 99—101°, was collected (crop A, 2·12 g.). The filtrate, together with the methanol washings (10 c.c.) of crop A, was diluted with water (10 c.c.) and again cooled overnight, giving a further quantity of solid (crop B, 1·62 g.), m. p. below 75°. Two further dilutions with water (10 c.c. and 5 c.c.) gave more crystalline solid of low m. p. (crop C, 0·51 g.; crop D, 0·46 g.). The final mother-liquors gave only oily material on dilution with water.

Crop A, on recrystallisation from aqueous methanol, gave pale yellow needles of $\Delta^{2:9(14)}$-*decahydro*-1 : 4-*diketo*-2(or 3)-*methylphenanthrene* (XIX), m. p. 100—102° (Found: C, 77·8; H, 8·0. $C_{15}H_{18}O_2$ requires C, 78·2; H, 7·9%). Crops B, C, and D were combined, and, after several crystallisations from aqueous methanol, gave pale yellow prisms, m. p. 94—95°, depressed to 68—90° on admixture with the needles of m. p. 100—102° (above). This material, m. p. 94—95°, was doubtless the isomeric *decahydrodiketomethylphenanthrene* (XIX) (Found: C, 77·8; H, 7·9. $C_{15}H_{18}O_2$ requires C, 78·2; H, 7·9%).

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