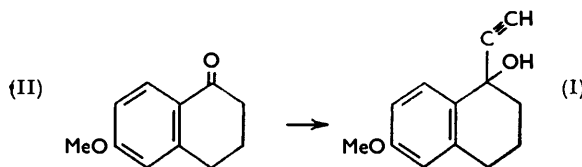


**632. Studies on the Diels-Alder Reaction. Part IV.\* Reduction Products of *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Octahydro-8-methoxy-1 : 4-dioxochrysene and their Interrelation.**

By P. A. ROBINS and JAMES WALKER.

1-Ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene (I), derived from the tetralone (II), has been converted by partial hydrogenation and dehydration into 3:4-dihydro-6-methoxy-1-vinylnaphthalene, which, on addition of *p*-benzoquinone, afforded *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1:4-dioxochrysene (III). Partial reductions and stereochemical transformations of the type previously applied in the hydrophenanthrene series<sup>1a, b</sup> have been applied to this compound, and the structures of the products are demonstrated.

THE work described in the present communication was carried out in the course of extending our previous study<sup>1</sup> of perhydro-1 : 4-dioxophenanthrenes and related compounds to the chrysene series. For this purpose it was fortunate that a recent patent<sup>2</sup> has reported that 1-ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene (I) is obtainable in good yield by the reaction between 1 : 2 : 3 : 4-tetrahydro-6-methoxy-1-oxonaphthalene (II) and lithium acetylide in liquid ammonia at room temperature in a sealed vessel. Previous attempts to prepare the acetylenic alcohol (I) by reaction between the tetralone (II) and sodium or potassium acetylide have failed,<sup>3</sup> or have given moderate yields only,<sup>4</sup> while the use of ethynylmagnesium bromide<sup>5, 6</sup> has allowed the preparation of small quantities of impure material to be undertaken with great experimental difficulty, and the formation of considerable amounts of disubstituted acetylene,  $>C(OH)\cdot C\equiv C(OH)<$  or  $\geq C\cdot C\equiv C\leq$ , was also reported.<sup>3, 5, 6</sup> Using the lithium acetylide method we have been able to obtain consistent net yields of over 60% of the acetylenic alcohol (I) by careful attention to experimental detail, in particular by



ensuring the presence of a large excess of acetylene during the reaction stage at room temperature, the product being obtained crystalline. Previous workers<sup>5, 6</sup> who prepared this compound by the ethynylmagnesium bromide method found either that their crude products underwent spontaneous partial dehydration to the enyne or that distillation gave a partially dehydrated product with occasional polymerisation, and a similar result was reported for a preparation employing sodium acetylide in dioxan at 30–40°. <sup>4a</sup> We have found in contrast to these reports, and in agreement with Goldberg and Scott,<sup>2</sup> that the solid acetylenic alcohol (I) can be distilled unchanged, even at water-pump vacua (b. p. *ca.* 180°/15 mm.). Dehydration by chemical methods occurs readily but in most cases

\* Part III, *J.*, 1954, 3960.

<sup>1</sup> Robins and Walker, (a) *J.*, 1952, 642; (b) 1954, 3960; (c) 1955, 1789; (d) *Chem. and Ind.*, 1955, 772.

<sup>2</sup> Goldberg and Scott, U.S.P. 2,524,787.

<sup>3</sup> Birch and Robinson, *J.*, 1944, 503.

<sup>4</sup> Breitner, (a) in "Pharmaceuticals at the I.G. Farbenindustrie Plant, Elberfeld, Germany," C.I.O.S. Report, Item 24, File XXV-54, p. 20 (35% yield); (b) *Medizin und Chemie*, 1942, 4, 317; (c) Wunderlich, Dissertation, Wurzburg, 1939, quoted by Buchta and Bayer, *Annalen*, 1953, 580, 117.

<sup>5</sup> (a) Dane, Höss, Bindseil, and Schmitt, *Annalen*, 1937, 532, 39; (b) Dane, Höss, Eder, Schmitt, and Schön, *ibid.*, 1938, 536, 183.

<sup>6</sup> (a) Goldberg and Müller, *Helv. Chim. Acta*, 1940, 23, 831; (b) Bachmann and Chemerda, *J. Amer. Chem. Soc.*, 1948, 70, 1468; (c) Bachmann and Controulis, *ibid.*, 1951, 73, 2636; (d) Nazarov and Kotlyarevskii, *Bull. Acad. Sci. U.S.S.R. (Sect. Chem. Sci.)*, 1953, 1100.

rapid polymerisation of the resulting product takes place. The Hibbert method,<sup>7</sup> employing iodine in boiling benzene, failed; the use either of thionyl chloride or of phosphoryl chloride in pyridine resulted in a violent reaction and the production of resin; toluene-*p*-sulphonic acid or anhydrous oxalic acid in boiling benzene, or acetic anhydride-sulphuric acid gave only tars. The use of acetic anhydride under reflux<sup>4a</sup> was also unsatisfactory. Alone among the methods employed, rapid distillation on a small scale from fused potassium hydrogen sulphate gave an oil, which, on subsequent partial hydrogenation and reaction with *p*-benzoquinone, gave a quantity of the chrysene derivative (III) indicating that the initial dehydration had given at least 60% of 1-ethynyl-3 : 4-dihydro-6-methoxynaphthalene.

Alternatively, partial hydrogenation of the acetylenic alcohol (I) with the Lindlar<sup>8</sup> lead-poisoned palladised calcium carbonate catalyst gave smoothly 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxy-1-vinylnaphthalene, which could be distilled in small quantities without undergoing dehydration. Attempted dehydration under acid conditions gave only polymeric material, but, in this instance, the Hibbert method<sup>7</sup> was successful when a basic polymerisation-inhibitor, such as quinoline or phenyl- $\beta$ -naphthylamine, was present. Attempts to isolate the resulting 3 : 4-dihydro-6-methoxy-1-vinylnaphthalene indicated that it readily polymerised,<sup>9</sup> and it was best allowed to react directly in benzene solution at room temperature with *p*-benzoquinone to give the desired *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1 : 4-dioxochrysene (III) in 70% yield [based on the acetylenic alcohol (I)]; this substance (III) has been prepared by Dane *et al.*<sup>5</sup> in unspecified yield, but it has not previously been studied in detail.

The *cis-syn*-configuration is assigned to the compound (III) on the basis of the Alder-Stein<sup>10</sup> rules for diene additions. When it (III) was cautiously treated under nitrogen with alcoholic alkali, aromatisation of the ring containing the two carbonyl groups took place and the product, 5 : 6 : 12 : 15-tetrahydro-1 : 4-dihydroxy-8-methoxychrysene (IV), showed in its ultraviolet absorption spectrum (Fig. 1) two bands characteristic of the two isolated chromophores—one at 265 m $\mu$ , characteristic of a methoxystyrene chromophore of the type incorporated in (IV) (see below), and a typical quinol band at 295 m $\mu$ . Treatment of the diketone (III) with hydrogen bromide in acetic acid, however, gave an isomeric structure having an ultraviolet absorption spectrum (Fig. 1) with a broad band showing signs of resolution in the 330—340 m $\mu$  region, and obviously having the conjugated *trans*-stilbene-like structure of 5 : 6 : 11 : 12-tetrahydro-1 : 4-dihydroxy-8-methoxychrysene (V). The same substance (V) was also rapidly produced on treatment of the alkali-isomerisation product (IV) in hot benzene with a drop of acetic acid containing hydrogen bromide. The 11 : 16-double bond in (III) was stable in the presence of acetic acid, and reduction of (III) with zinc and acetic acid removed the 2 : 3-double bond to give *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (VI) showing a maximum in its ultraviolet absorption spectrum at 264 m $\mu$  (Fig. 2). The 11 : 16-double bond in (VI), however, was labile in presence of mineral acid and readily migrated into the 15 : 16-position to give *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (VII), showing a maximum in its ultraviolet absorption spectrum at 273.5 m $\mu$  (Fig. 2), the shift in the position of maximum absorption being accompanied by a slight drop in the extinction coefficient. The position of the maximum observed for this compound (VII) agrees well with other data reported for 3 : 4-dihydro-6-methoxynaphthalenes,<sup>11</sup> and, in particular, the shift in the position of maximum absorption to longer wavelength in passing from (VI) to (VII) is in accord with previous experience of analogous structures,<sup>11b,d</sup> especially with the observations of Heer and Miescher<sup>11b</sup> on the change in ultraviolet light absorption in passing from (VIII) to (IX). Although the shift is small the position of maximum absorption in this group of substances is diagnostic of the position

<sup>7</sup> Hibbert, *J. Amer. Chem. Soc.*, 1915, **37**, 1748.

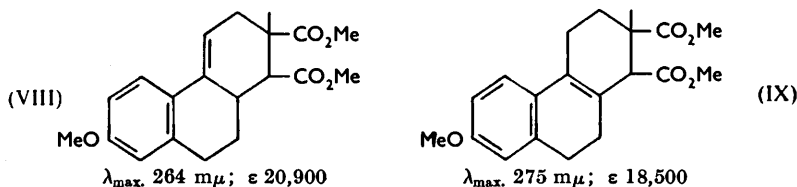
<sup>8</sup> Lindlar, *Helv. Chim. Acta*, 1952, **35**, 440.

<sup>9</sup> Cf. Buchta and Bayer, *Annalen*, 1953, **580**, 116.

<sup>10</sup> Alder and Stein, *Angew. Chem.*, 1937, **50**, 510.

<sup>11</sup> (a) Woodward and Eastman, *J. Amer. Chem. Soc.*, 1944, **66**, 674; (b) Heer and Miescher, *Helv. Chim. Acta*, 1948, **31**, 219; (c) Hogg, *J. Amer. Chem. Soc.*, 1949, **71**, 1918; (d) Juday, *ibid.*, 1953, **75**, 3008.

of the olefinic double bond, as further examples will show later; it does not, of course, apply when the methoxystyrene chromophore is conjugated with another chromophore,



as in (V) (above). During the acid isomerisation of (VI) to (VII) in ethanolic hydrochloric acid, the formation of a by-product  $C_{21}H_{22}O_2$  in about 20% yield was observed, and with methanolic hydrochloric acid a similar by-product  $C_{20}H_{20}O_2$ , containing two methoxyl

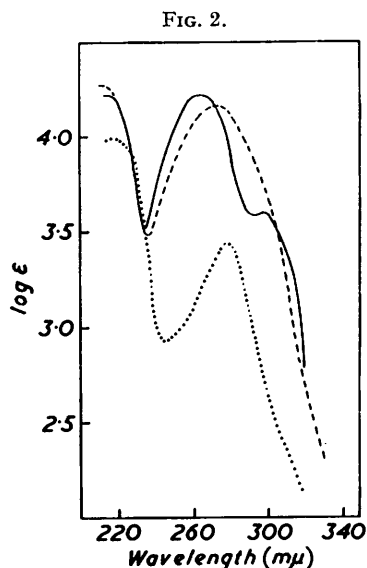
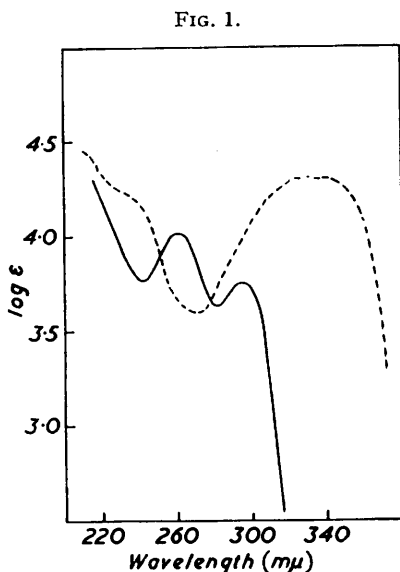


FIG. 1. Ultraviolet light absorption of 5:6:12:15-tetrahydro-1:4-dihydroxy-8-methoxychrysene (IV) (—), and 5:6:11:12-tetrahydro-1:4-dihydroxy-8-methoxychrysene (V) (---).

FIG. 2. Ultraviolet light absorption of *cis-syn*-1:2:3:4:5:6:12:13:14:15-decahydro-8-methoxy-1:4-dioxochrysene (VI) (—), *cis*-1:2:3:4:5:6:11:12:13:14-decahydro-8-methoxy-1:4-dioxochrysene (VII) (---), and *cis-syn-cis*-1:2:3:4:5:6:11:12:13:14:15:16-dodecahydro-8-methoxy-1:4-dioxochrysene (X) (· · ·).

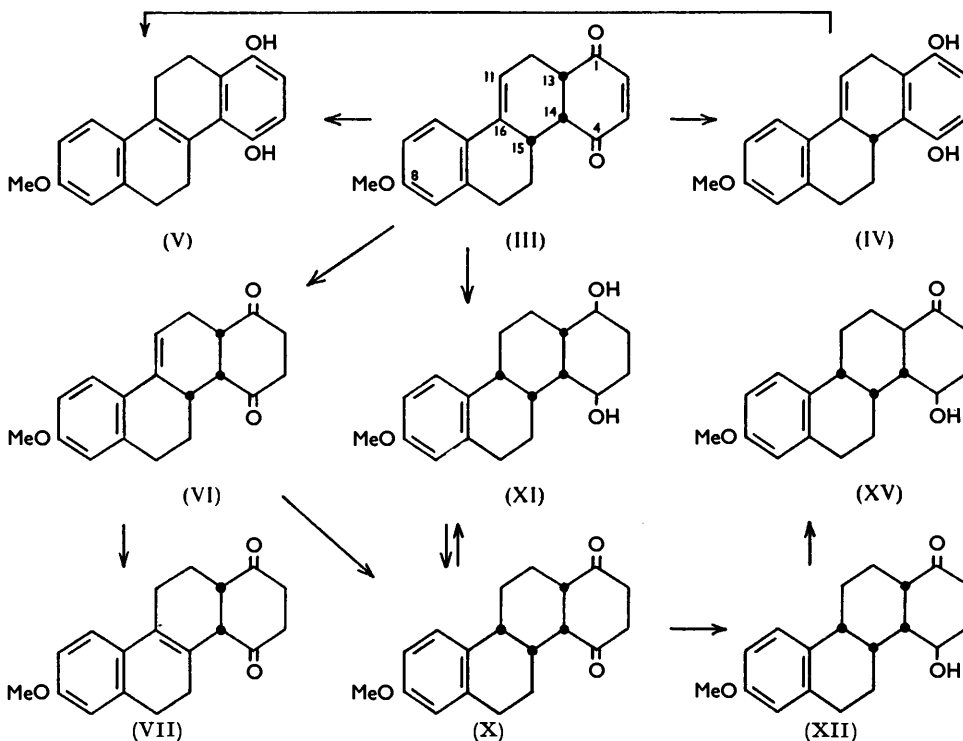
groups, was obtained. The ultraviolet light absorption characteristics of these two substances were virtually indistinguishable and indicated that a radical change in structure had occurred. The two methoxyl groups in the latter compound accounted for the two oxygen atoms, and the substances were obviously derived from (VI), or from (VII), by the loss of the elements of two molecules of water and the addition of the elements of the alcohol employed. The structures and mode of formation of these compounds will be discussed in the following paper.

The *cis-syn*-diketone (VI) on catalytic hydrogenation in the presence of palladised strontium carbonate took up one mol. of hydrogen to give *cis-syn-cis*-1:2:3:4:5:6:11:12:13:14:15:16-dodecahydro-8-methoxy-1:4-dioxochrysene (X), since catalyst hindrance<sup>12</sup> would have effectively prevented the formation of the alternative *cis-syn-trans*-structure, and this substance (X) proved to be rather unstable to heat, partly decomposing to a yellow gum on crystallisation from hot solvents. By keeping the

<sup>12</sup> Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

time of heating to a minimum or by recrystallisation in the cold by the slow addition of light petroleum to a chloroform solution of the compound, it could be obtained in the form of prisms, m. p. 159—164° (decomp.); the ultraviolet light absorption (Fig. 2) was of the anisole type. Dane *et al.*<sup>55</sup> report the isolation of two unstable products on catalytic hydrogenation of the original adduct (III) in anisole solution in the presence of palladised calcium carbonate or palladised charcoal, having m. p. 130—132° and 145—148° respectively. These may have been impure specimens of the substance (X), since no pure compounds of such low melting point were encountered in the present work.

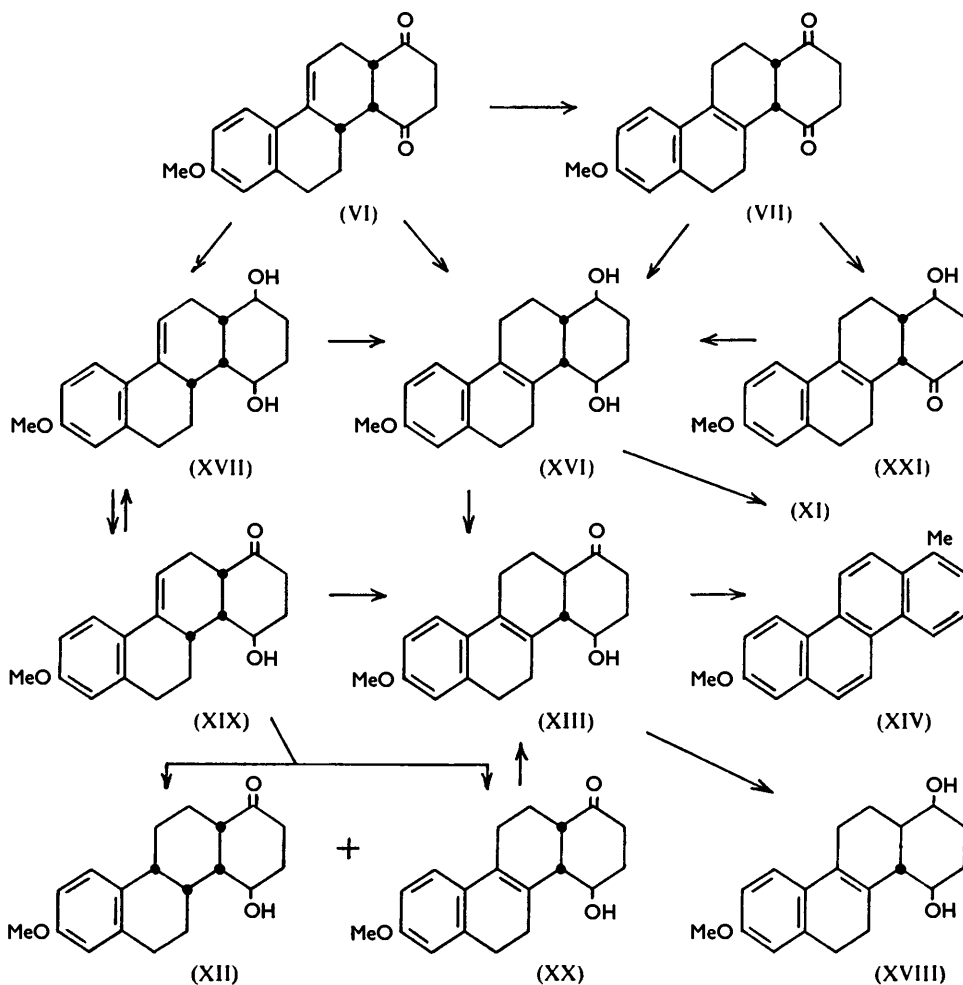
Reduction of the *cis-syn-cis*-diketone (X) with lithium aluminium hydride afforded a *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-1 : 4-dihydroxy-8-methoxychrysene (XI), identical with the diol obtained directly by catalytic hydrogenation of the original adduct (III) in glacial acetic acid in the presence of Adams's platinum oxide



catalyst, thus indicating the stereochemical course of the reduction of the carbonyl groups to be the same in both cases. This diol (XI) showed a double melting point at 158—161° and 170—173°, and was probably identical with the dihydroxy-compound, m. p. 163°, reported by Dane *et al.*<sup>55</sup> from a similar catalytic reduction of the adduct (III). The products, allegedly formed by reductive demethoxylation, of m. p. 194° and 183—184° obtained by Dane *et al.*<sup>55</sup> on catalytic hydrogenation of (III) with platinum in acetic acid and anisole respectively were not encountered during the present investigation. Catalytic hydrogenation of the *cis-syn-cis*-diketone (X) in ethyl acetate in the presence of Adams's platinum oxide catalyst resulted in the uptake of one mol. of hydrogen and production of a hydroxy-ketone. On the basis of experience in the perhydrophenanthrene series<sup>1a, b</sup> this substance should have been *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysene (XII), and this structure was subsequently proved (see below) by correlation of (XII) with a hydroxy-ketone (XIII) which was converted into 8-methoxy-1-methylchrysene (XIV). The *cis-syn-cis*-hydroxy-ketone (XII) was stereochemically unstable and was readily converted on treatment with alcoholic

alkali into the more stable *trans-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XV). *cf. 1a, b*

Reduction of the *cis-syn*-diketone (VI) with lithium aluminium hydride afforded two alternative products according to the experimental conditions. Reduction under vigorous conditions in boiling tetrahydrofuran, followed by decomposition of the reaction mixture with water and mineral acid, gave a diol of m. p. 152—156°. As the same substance was obtained by reduction of the *cis*-diketone (VII) with lithium aluminium hydride and as it showed a maximum in its ultraviolet light absorption at 273 m $\mu$ , it must have had the olefinic double bond in the 15 : 16-position and was therefore *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dihydroxy-8-methoxychrysenes (XVI); it passed into the *cis-syn-cis*-diol (XI), showing the characteristic double melting point described above, on catalytic hydrogenation in acetic acid in presence of Adams's platinum



oxide catalyst. On the other hand reduction of the *cis-syn*-diketone (VI) with lithium aluminium hydride in cold tetrahydrofuran (or with but a brief period of heating) followed by a working-up procedure not involving the use of acid gave a diol, isomeric with (XVI), of m. p. 183—185°; it showed a maximum in its ultraviolet light absorption at 265 m $\mu$  and was obviously *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-1 : 4-dihydroxy-8-methoxychrysenes (XVII). The olefinic double bond in the 11 : 16-position in this substance (XVII), as in other instances noted above, was labile in presence of mineral acid, and brief

treatment of (XVII) with alcoholic hydrochloric acid effected complete conversion into the isomeric  $\Delta^{15:16}$ -*cis*-diol (XVI).

Partial oxidation of either the  $\Delta^{15:16}$ -*cis*-diol (XVI) or the  $\Delta^{11:16}$ -*cis-syn*-diol (XVII) with the chromium trioxide-pyridine reagent<sup>1b,13</sup> failed to give any recognisable product other than some unchanged starting material, but Oppenauer oxidation gave in each case a hydroxy-ketone with retention of the original position of the olefinic double bond as shown by the ultraviolet light absorption. The carbonyl group introduced by the Oppenauer reaction should, by analogy with experience in the hydrophenanthrene series,<sup>1b</sup> be at C<sub>(1)</sub>, and confirmation of this was obtained by marking the position of the carbonyl group in the hydroxy-ketone, m. p. 177—179°, derived from the  $\Delta^{15:16}$ -*cis*-diol (XVI), with methylmagnesium iodide, followed by dehydration and dehydrogenation to give 8-methoxy-1-methylchrysene (XIV), identical with an authentic synthetic specimen (see following paper). Moreover, reduction of the hydroxy-ketone, m. p. 177—179°, with lithium aluminium hydride gave, not its precursor (XVI), but a new stereoisomeric diol, indicating inversion to have taken place adjacent to the carbonyl group introduced during the Oppenauer oxidation in a similar fashion to that observed previously in analogous cases.<sup>1b,13</sup> The hydroxy-ketone, m. p. 177—179°, derived from the  $\Delta^{15:16}$ -*cis*-diol (XVI) was therefore *trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XIII), affording *trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVIII) on reduction. The hydroxy-ketone, m. p. 191—194°, obtained by Oppenauer oxidation of the  $\Delta^{11:16}$ -*cis-syn*-diol (XVII) was converted into the isomeric hydroxy-ketone (XIII), derived from the  $\Delta^{15:16}$ -*cis*-diol, by treatment with ethanolic hydrochloric acid. That this isomerisation does not solely involve a migration of the olefinic double bond is, however, apparent from the fact that the hydroxy-ketone, m. p. 191—194°, on reduction with lithium aluminium hydride regenerates its precursor (XVII) and thus retains the *cis-syn*-configuration. It is therefore *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XIX), and its conversion into (XIII) by the action of acid involves inversion at C<sub>(13)</sub> as well as the shift of the double bond. The formation of this *cis-syn*-hydroxy-ketone (XIX) in the Oppenauer oxidation of the *cis-syn*-diol (XVII) is noteworthy, since in previous cases involving the oxidation of *cis*-fused 1 : 4-diols,<sup>1b,13</sup> and in the one noted above [(XVI) → (XIII)], the conditions of this reaction have been found to effect stereochemical inversion of configuration at labile centres adjacent to the newly introduced carbonyl group. The stereochemical stability of (XIX), however, was confirmed by its substantial recovery from treatment with cold alcoholic sodium ethoxide or boiling alcoholic potassium hydroxide.

A further correlation of structures was obtained by the catalytic hydrogenation of the *cis-syn*-hydroxy-ketone (XIX) in the presence of palladised strontium carbonate to give a mixture of two products, which were separated with some difficulty and were not obtained absolutely pure. One was *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysene (XII), identical with the substance obtained on catalytic hydrogenation of the *cis-syn-cis*-diketone (X), and this observation incidentally confirms the assignment of the 4-hydroxy-1-oxo-structure to (XII) as prepared above from (X). The other product was shown by its ultraviolet light absorption to belong to the  $\Delta^{15:16}$ -series of compounds, and was obviously formed from (XIX) by a shift of the double bond under the influence of the palladium catalyst of the type noted previously;<sup>1b</sup> it was, in fact, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XX), which is more fully characterised in the following paper, and it was readily converted on treatment with alcoholic alkali (see next paper) into the *trans*-compound (XIII). A new  $\Delta^{15:16}$ -hydroxy-ketone, m. p. 167—168°, was obtained on catalytic hydrogenation of the  $\Delta^{15:16}$ -*cis*-diketone (VII) in the presence of palladised strontium carbonate. As it could be further reduced with lithium aluminium hydride to give the  $\Delta^{15:16}$ -*cis*-diol (XVI), and since it differed from the  $\Delta^{15:16}$ -*cis*-hydroxy-ketone (XX) but nevertheless contained the hydroxyl group in the same absolute configuration as one of those present in (XVI), it must have been the isomeric *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1-hydroxy-8-methoxy-4-oxochrysene (XXI).

<sup>1b</sup> Poos, Arth, Beyler, and Sarett, *ibid.*, 1953, **75**, 422.

It decomposed when heated with alcoholic alkali in an attempt to convert it into the *trans*-stereoisomer, but it was stable to adsorption on to, and desorption from, alkaline alumina. Treatment with perchloric acid in ethyl acetate, previously used<sup>1b</sup> with success for the stereochemical equilibration of diketones in the hydrophenanthrene series, merely gave the acetate of (XXI).

#### 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. Ultraviolet light absorption measurements were made in 96% EtOH unless otherwise stated. Light petroleum refers to the fraction of boiling range 60—80°.

1-Ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene (I) (cf. ref. 2).—A solution of lithium acetylde (from 3.82 g. of lithium) in liquid ammonia (ca. 800 c.c.) was transferred to the glass liner of a mild-steel bomb (capacity, 1700 c.c.), cooled in solid carbon dioxide. A rapid stream of acetylene was passed for 20 min., and then 1 : 2 : 3 : 4-tetrahydro-6-methoxy-1-oxonaphthalene (44 g., 0.25 mole) was added as powder. The glass liner was immediately placed in the chilled bomb which was then sealed. After warming to room temperature the bomb was rotated in an inclined position for 20 hr. Excess of acetylene and ammonia were then vented, the bomb was opened, and the brown pasty residue was treated with solid ammonium chloride (30 g.), followed by ether and water. The ether layer was separated, washed successively with water, dilute sulphuric acid (until free from ammonia), and water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated in an atmosphere of carbon dioxide. The residual dark oil, or pasty solid, was taken up in benzene (50 c.c.), diluted with light petroleum (50 c.c.), and allowed to crystallise at 0°. Filtration then afforded 1-ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene (I) as brownish prisms (24.5 g.), m. p. 88—89°, sufficiently pure for use in subsequent stages; the m. p. was not raised on recrystallisation from benzene-light petroleum (Found : C, 77.3; H, 7.1. Calc. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub> : C, 77.2; H, 7.0%). Goldberg and Scott<sup>2</sup> record m. p. 89°.

The mother-liquors were evaporated to dryness and the residue was treated at 50° with semicarbazide (from 20 g. of semicarbazide hydrochloride neutralised by aqueous sodium hydroxide) and acetic acid (1 c.c.) in 85% aqueous methanol (400 c.c.). After 20 hr. the precipitated 1 : 2 : 3 : 4-tetrahydro-6-methoxy-1-oxonaphthalene semicarbazone (7.6 g.) was collected and the filtrate was poured into much water. Extraction with ether and evaporation of the washed and dried extract gave an oily residue (7.7 g.), which was dissolved in benzene (10 c.c.) and diluted with light petroleum (10 c.c.) to yield a further crop (3.6 g.; m. p. 86—88°) of 1-ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene.

1 : 2 : 3 : 4-Tetrahydro-1-hydroxy-6-methoxy-1-vinylnaphthalene.—1-Ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene (5.75 g.) was shaken in dry ether (50 c.c.) in hydrogen at room temperature and atmospheric pressure in the presence of the Lindlar<sup>8</sup> catalyst (0.2 g.) but without the usual addition of quinoline as a catalyst inhibitor. Absorption of hydrogen ceased after the uptake of approx. 1 mol. in ca. 4 hr. Removal of the catalyst and distillation afforded 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxy-1-vinylnaphthalene as a colourless viscous oil (5.4 g.), b. p. 106—110°/0.01 mm., *n*<sub>D</sub><sup>23</sup> 1.5648 (Found : C, 76.8; H, 7.7. C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> requires C, 76.5; H, 7.9%). Distillation of large quantities of this substance was unsatisfactory, dehydration and polymerisation frequently occurring, particularly when an acid washing had been used to remove quinoline in experiments in which it had been included.

*cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Octahydro-8-methoxy-1 : 4-dioxochrysene (III).—1-Ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene (25.9 g.) was hydrogenated as above with the addition of quinoline (0.2 c.c.) which was not removed subsequently, and the crude 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxy-1-vinylnaphthalene was heated with a crystal of iodine in benzene (80 c.c.) under reflux with the conventional Dean and Stark apparatus. Separation of water took place rapidly during the first few minutes of heating and practically ceased in 20 min. (Found : 2.05 c.c. Calc. : 2.4 c.c.). The benzene solution of 3 : 4-dihydro-6-methoxy-1-vinylnaphthalene was cooled rapidly to room temperature and *p*-benzoquinone (13.8 g., 1 mol.) was added, and brought into solution by swirling. The clear brown solution was set aside at room temperature in the dark. A crystalline mass commenced to separate within  $\frac{1}{2}$  hr. from the then warm solution. After 20 hr. methanol (80 c.c.) was added, the crystalline material was broken up, filtered, and washed with methanol, to give pale yellow needles (24.6 g.) of *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1 : 4-dioxochrysene, m. p. 152—156°. A further crop (2.6 g.) could be obtained by evaporation of the mother-liquors and washings to small bulk. The m. p. was raised to 161° (decomp.) by

recrystallisation from benzene–light petroleum (Found : C, 77.5; H, 6.4. Calc. for  $C_{19}H_{18}O_3$  : C, 77.6; H, 6.1%). Dane *et al.*<sup>5b</sup> record m. p. 160–161° (decomp.).

*Aromatisation of cis-syn-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Octahydro-8-methoxy-1 : 4-dioxochrysenes* (III).—(a) *By acid.* Formation of 5 : 6 : 11 : 12-tetrahydro-1 : 4-dihydroxy-8-methoxychrysenes (V). *cis-syn-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Octahydro-8-methoxy-1 : 4-dioxochrysenes* (2.0 g.), suspended in acetic acid (50 c.c.), was treated with a 50% solution of hydrogen bromide in acetic acid (5 c.c.). The solid immediately dissolved and a greenish colour was produced. After a few minutes the colour changed to blue-black, and the solution showed a strong fluorescence in ultraviolet light. After 2 hr. at room temperature, when the colour had faded to pale violet, the solution was poured into water, and the precipitated blue-grey solid was collected. Crystallisation from toluene afforded 5 : 6 : 11 : 12-tetrahydro-1 : 4-dihydroxy-8-methoxychrysenes (V) (1.41 g.) in greyish-white leaflets, m. p. (micro) 201–204°, rapidly becoming blue-grey (Found : C, 77.1; H, 6.4.  $C_{19}H_{18}O_3$  requires C, 77.6; H, 6.1%). The presence of the 15 : 16-olefinic double bond was indicated by the ultraviolet light absorption :  $\lambda_{max}$ , ca. 207, 327, and 339 m $\mu$  (log  $\epsilon$  4.46, 4.30, and 4.31 respectively) (Fig. 1). The substance gave a Burgundy-red colour with ferric chloride in methanol, changing to bluish-purple on dilution with water.

(b) *By alkali.* Formation of 5 : 6 : 12 : 15-tetrahydro-1 : 4-dihydroxy-8-methoxychrysenes (IV). A solution of *cis-syn-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1 : 4-dioxochrysenes* (0.5 g.) and sodium acetate (0.5 g.) in warm ethanol (100 c.c.) was treated under nitrogen with *n*-sodium hydroxide (5 c.c.). As soon as the solutions had mixed, *n*-hydrochloric acid (5.5 c.c.) was added to neutralise the alkali. The product, isolated by dilution with water and extraction with chloroform, was recrystallised from benzene, affording 5 : 6 : 12 : 15-tetrahydro-1 : 4-dihydroxy-8-methoxychrysenes (IV) in needles, m. p. (micro) 110–115° and, after resolidification, 175–182° (decomp.), rapidly darkening (Found : C, 77.3; H, 6.1%). The presence of the olefinic 11 : 16-double bond was indicated by the ultraviolet light absorption :  $\lambda_{max}$ , 261 and 294 m $\mu$  (log  $\epsilon$  4.02 and 3.76) (Fig. 1). The substance gave no colour with ferric chloride in methanol.

*Acid Isomerisation of 5 : 6 : 12 : 15-Tetrahydro-1 : 4-dihydroxy-8-methoxychrysenes* (IV).—The substance (IV) (100 mg.), dissolved in hot benzene (5 c.c.), was treated with one drop of a 50% solution of hydrogen bromide in glacial acetic acid. After 1 min. the clear solution was seeded with the  $\Delta^{15:16}$ -isomer and crystallisation commenced. At the end of 1 hr. filtration afforded 5 : 6 : 11 : 12-tetrahydro-1 : 4-dihydroxy-8-methoxychrysenes (V) (80 mg.), m. p. (micro) 201–205°, not depressed on admixture with the specimen prepared, as above, directly from the diketone (III).

*cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-8-methoxy-1 : 4-dioxochrysenes* (VI).—*cis-syn-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Octahydro-8-methoxy-1 : 4-dioxochrysenes* (III) (9.0 g.), dissolved in acetic acid (450 c.c.) by gentle warming and then cooled to ca. 25°, was treated with zinc powder (9 g.), added in several portions with shaking and water-cooling during 3–4 min. A second portion of zinc powder (9 g.) was then added all at once and shaking was continued for a further 5 min.; cooling was not usually necessary during this second addition. The product separated during the reduction as a fine crystalline suspension. The reaction mixture was poured into water (1.5 l.) and extracted three times with chloroform, each extract being filtered as rapidly as possible from entrained zinc. The combined chloroform extracts were washed with water, with dilute aqueous sodium hydrogen carbonate solution, and again with water, and evaporated under reduced pressure until crystals began to separate. Crystallisation was completed by the addition of methanol to give *cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysenes* (VI) as needles (7.5 g.), m. p. 194–196° (decomp.); a further quantity (0.97 g.) was obtained from the mother-liquors on evaporation (Found : C, 77.3; H, 6.7.  $C_{19}H_{20}O_3$  requires C, 77.0; H, 6.8%). The presence of the olefinic 11 : 16-double bond was indicated by the ultraviolet light absorption :  $\lambda_{max}$ , 264 and 299 m $\mu$  (log  $\epsilon$  4.23 and 3.60) (Fig. 2).

*Acid Isomerisation of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-8-methoxy-1 : 4-dioxochrysenes* (VI). *cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-Decahydro-8-methoxy-1 : 4-dioxochrysenes* (VII).—*cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-8-methoxy-1 : 4-dioxochrysenes* (1.0 g.) was dissolved in a warm mixture of ethanol (50 c.c.) and chloroform (30 c.c.), and the solution was heated under reflux with concentrated hydrochloric acid (4 c.c.) for 30 min. A clear yellow colour rapidly developed. Distillation of part of the solvent (to remove the chloroform) gave a clear yellow solution which was cooled and diluted with water to cloudiness. The crystals (180 mg.) which separated were collected, and recrystallisation from ethanol gave a compound,  $C_{21}H_{22}O_2$ , as white needles, m. p. (micro) 119–120.5°, which lacked ketonic properties



(Found: C, 82.2; H, 7.2.  $C_{21}H_{22}O_2$  requires C, 82.3; H, 7.2%). Ultraviolet light absorption in hexane:  $\lambda_{\max}$ , 316, 330, and 346  $m\mu$  ( $\log \epsilon$  4.38, 4.44, and 4.29 respectively).

The reaction mixture, after separation of the compound  $C_{21}H_{22}O_2$ , was poured into water and extracted twice with chloroform. The combined extracts, washed with water, dried, and evaporated, gave a solid residue, which, after several crystallisations from ethanol, gave *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysenes (VII) as flattened pale yellow needles (0.3 g.), m. p. (micro) 154–157° (decomp.) (Found: C, 77.3; H, 6.9.  $C_{19}H_{20}O_3$  requires C, 77.0; H, 6.8%). The presence of the olefinic 15 : 16-double bond was indicated by the ultraviolet light absorption:  $\lambda_{\max}$ , 273.5  $m\mu$  ( $\log \epsilon$  4.16) (Fig. 2). Reduction of this substance (VII) (100 mg.) with lithium aluminium hydride in tetrahydrofuran gave the *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dihydroxy-8-methoxychrysenes (XVI) described below (70 mg.), m. p. and mixed m. p. (micro) 150–152.5°.

Repetition of the acid isomerisation of *cis*-*syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysenes (VI) but employing methanol as the sole solvent gave again a mixture. The main product was *cis*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysenes (VII) as before, but the minor product was a *compound*, m. p. (micro) 125–127°, depressed on admixture with the compound  $C_{21}H_{22}O_2$  (above) (m. p. 119–120.5°) (Found: C, 82.2; H, 6.9; OMe, 21.7.  $C_{20}H_{20}O_2$  requires C, 82.2; H, 6.9; 2OMe, 21.2%). The ultraviolet light absorption characteristics of this substance closely resembled those of the  $C_{21}$  compound.

*cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-Dodecahydro-8-methoxy-1 : 4-dioxochrysenes (X).—*cis*-*syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-8-methoxy-1 : 4-dioxochrysenes (VI) (1.0 g.), suspended in ethanol (100 c.c.), was hydrogenated at room temperature and atmospheric pressure in the presence of 2% palladised strontium carbonate (1 g.). Absorption of hydrogen ceased after 4 hr. (uptake, 0.93 mol.). Removal of the catalyst and evaporation to small bulk under reduced pressure with gentle warming gave colourless prisms (0.73 g.), m. p. (micro) 153–163°; the yellow mother-liquors gave only gum on evaporation. Recrystallisation of the solid product from ethanol–chloroform left, on each occasion, yellow decomposition products in the mother-liquor, with *cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysenes (X) separating in prisms, m. p. (micro) 160–165° (decomp.) (Found: C, 76.5; H, 7.7.  $C_{19}H_{22}O_3$  requires C, 76.5; H, 7.4%). Ultraviolet light absorption:  $\lambda_{\max}$ , 280  $m\mu$  ( $\log \epsilon$  3.44) (Fig. 2).

*cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-Dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XII).—*cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-Dodecahydro-8-methoxy-1 : 4-dioxochrysenes (X) (0.75 g.) in ethyl acetate (100 c.c.) was hydrogenated at room temperature and atmospheric pressure in the presence of Adams platinum oxide catalyst (100 mg.). Approx. 1 mol. of hydrogen was absorbed in 28 hr. and crystals separated. After the addition of some chloroform to effect complete solution, the catalyst was removed and the solvent was evaporated under reduced pressure. Crystallisation of the solid residue from chloroform–ethanol gave *cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XII) as prisms (0.60 g.), m. p. (micro) 205–208° (Found: C, 75.8; H, 8.1.  $C_{19}H_{24}O_3$  requires C, 76.0; H, 8.1%).

*trans*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-Dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XV).—*cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-Dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XII) (0.68 g.) was heated under reflux for 1 hr. in 1% ethanolic potassium hydroxide (80 c.c.), and the solution was then cooled and poured into an excess of dilute aqueous hydrochloric acid. The precipitated solid was collected, and recrystallisation from *isobutyl* alcohol afforded colourless prisms (0.54 g.) of *trans*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes, (XV), m. p. (micro) 221–224° (Found: C, 75.8; H, 8.1.  $C_{19}H_{24}O_3$  requires C, 76.0; H, 8.1%).

*cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-Dodecahydro-1 : 4-dihydroxy-8-methoxychrysenes (XI).—(a) *By catalytic hydrogenation* of *cis*-*syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1 : 4-dioxochrysenes (III). The diketone (III) (1.0 g.) in glacial acetic acid (100 c.c.) was hydrogenated at room temperature and atmospheric pressure in the presence of Adams' platinum oxide catalyst (150 mg.), the reduction being interrupted when the uptake of hydrogen amounted to 4 mols. Removal of the catalyst and distillation under reduced pressure gave a solid residue, affording, after several crystallisations from benzene–light petroleum or from ethyl acetate, *cis*-*syn*-*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-1 : 4-dihydroxy-8-methoxychrysenes (XI) as needles, m. p. (micro) 155° (transition), 169–172° (Found: C, 75.5; H, 8.5. Calc. for  $C_{19}H_{26}O_3$ : C, 75.5; H, 8.7%). Oxidation with chromium trioxide (2.5 equiv.)

in acetic acid gave *cis-syn-cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16*-dodecahydro-8-methoxy-1 : 4-dioxochrysene (X) in poor yield (*ca.* 10%).

(b) *By reduction of cis-syn-cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16*-dodecahydro-8-methoxy-1 : 4-dioxochrysene (X) with lithium aluminium hydride. The diketone (X) (100 mg.) was heated under reflux in tetrahydrofuran (20 c.c.) with lithium aluminium hydride (400 mg.) for 1 hr. After destruction of excess of reagent with ethyl acetate, dilute sulphuric acid and chloroform were added, and the product was recovered from the organic phase in the usual way. Recrystallisation from ethyl acetate gave *cis-syn-cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16*-dodecahydro-1 : 4-dihydroxy-8-methoxychrysene (XI) (60 mg.), m. p. (micro) 158—161° and 170—173°, not depressed on admixture with a specimen prepared as in (a) (above).

*Reduction of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15*-Decahydro-8-methoxy-1 : 4-dioxochrysene (VI) with Lithium Aluminium Hydride.—(a) *cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14*-Decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVI). The diketone (VI) (0.5 g.) in warm tetrahydrofuran (50 c.c.) was added slowly to a suspension of lithium aluminium hydride (1.0 g.) in tetrahydrofuran (25 c.c.). After being heated for 1 hr. under reflux, the mixture was cooled and excess of reagent was destroyed by the addition of ethyl acetate. The inorganic material was then dissolved by the addition of excess dilute sulphuric acid with vigorous shaking. Finally chloroform was added and the product was isolated from the organic phase in the usual way. Crystallisation of the residue from ethyl acetate—light petroleum then gave *cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14*-decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVI) as colourless plates (0.48 g.), m. p. (micro) 152—156° (Found : C, 76.2; H, 7.9.  $C_{19}H_{24}O_3$  requires C, 76.0; H, 8.1%). The presence of the olefinic 15 : 16-double bond was indicated by the ultraviolet light absorption :  $\lambda_{max}$ , 273  $\mu$  ( $\log \epsilon$  4.23).

The substance (XVI) (200 mg.) was hydrogenated in glacial acetic acid (20 c.c.) at room temperature and atmospheric pressure in presence of Adams's platinum oxide catalyst (50 mg.) until 1 mol. of hydrogen had been absorbed. Removal of the catalyst and evaporation under reduced pressure gave a solid residue, which afforded, after two recrystallisations from ethyl acetate, *cis-syn-cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16*-dodecahydro-1 : 4-dihydroxy-8-methoxychrysene (XI) (90 mg.), m. p. and mixed m. p. (micro) 173—176°.

(b) *cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15*-Decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVII). The diketone (VI) (2.0 g.) in warm tetrahydrofuran (120 c.c.) was added slowly to a stirred slurry of lithium aluminium hydride (2.0 g.) in tetrahydrofuran (30 c.c.), cooled in an ice-bath. At the end of the addition the mixture was heated to boiling and then again cooled in ice. Water was cautiously added to decompose excess of reagent and then in sufficient amount to give a thick paste with the precipitated inorganic material, from which the organic layer was decanted. The solid residue left on evaporation was crystallised from ethanol—ethyl acetate, affording *cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15*-decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVII) (1.66 g.) as leaflets, m. p. (micro) 183—185° (Found : C, 76.3; H, 8.2%). Retention of the ethylenic 11 : 16-double bond was indicated by the ultraviolet light absorption :  $\lambda_{max}$ , 265 and 300  $\mu$  ( $\log \epsilon$  4.28 and 3.54).

A sample, heated under reflux for  $\frac{1}{2}$  hr. in a mixture of ethanol and concentrated hydrochloric acid (25 : 1), was completely transformed into the *cis*-isomer (XVI), m. p. (micro) 152—156°, described in (a) (above).

*Oppenauer Oxidation of cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14*-Decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVI). *trans-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14*-Decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XIII).—The diol (XVI) (1.0 g.) was heated under reflux in benzene (50 c.c.) and cyclohexanone (10 c.c.) with aluminium isopropoxide (1 g.) for 48 hr. After cooling, water (2 c.c.) was added, and the mixture was shaken and filtered. The filtrate was evaporated under reduced pressure, finally at 100°/0.1 mm., and the viscous residue was dissolved in a little methanol. The crystals which separated were twice recrystallised from ethyl acetate—light petroleum to give *trans-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14*-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XIII) as prisms (0.40 g.), m. p. (micro) 177—179° (Found : C, 76.5; H, 7.7.  $C_{19}H_{22}O_3$  requires C, 76.5; H, 7.6%). Ultraviolet light absorption :  $\lambda_{max}$ , 275  $\mu$  ( $\log \epsilon$  4.21).

The hydroxy-ketone (XIII) (100 mg.) in tetrahydrofuran (15 c.c.) was added to a slurry of lithium aluminium hydride (400 mg.) in tetrahydrofuran (5 c.c.) and the mixture was heated under reflux for 30 min. After cooling and decomposition of excess of reagent by water, chloroform and dilute sulphuric acid were added and the solid product was recovered from the organic phase in the usual way. Several recrystallisations from ethyl acetate then gave *trans-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14*-decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVIII), prisms, m. p. (micro) 220—224° (Found : C, 75.8; H, 7.9.  $C_{19}H_{24}O_3$  requires C, 76.0; H, 8.1%).

*Conversion of trans-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-Decahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XIII) into 8-Methoxy-1-methylchrysenes (XIV).*—The hydroxy-ketone (XIII) (0.5 g.) was added in warm benzene (50 c.c.) to methylmagnesium iodide (from 2.0 g. of magnesium) in boiling benzene (100 c.c.) and the mixture was refluxed for 29 hr. (total). After cooling in ice and decomposition of excess of reagent with ice-cold 3*N*-sulphuric acid, the organic layer was separated, and the aqueous phase was extracted once with benzene. The combined organic layers were washed with water and evaporated to give a solid non-ketonic residue, which was heated with powdered anhydrous potassium hydrogen sulphate (3.0 g.) in nitrogen at 180–200° for 30 min. After cooling, the cake was leached with water, and organic material was taken up in benzene. The benzene extract, washed and evaporated, gave a green oil, which was mixed with diphenylamine (10 g.) and palladised charcoal (1.0 g. of 10%) and dehydrogenated under reflux for 5 hr. After cooling, the reaction mixture was extracted with ether. The ethereal solution was filtered, saturated with dry hydrogen chloride, again filtered to remove the precipitated diphenylamine hydrochloride, and evaporated. Recrystallisation of the residue from benzene then afforded 8-methoxy-1-methylchrysenes (XIV), leaflets (70 mg.), m. p. (micro) 263–265° (after a transition to liquid crystals above 190°), not depressed on admixture with an authentic specimen prepared as described in the following paper and showing identical ultraviolet light absorption behaviour.

*Oppenauer Oxidation of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-1 : 4-dihydroxy-8-methoxychrysenes (XVII). cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XIX).*—The diol (XVII) (1.0 g.) was oxidised as described in the case of the isomeric  $\Delta^{15:16}$ -diol (XVI) (above). The solid which separated after treatment with methanol was twice crystallised from ethyl acetate–light petroleum, to give cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XIX), leaflets (0.26 g.), m. p. (micro) 191–194° (Found: C, 76.6; H, 7.6.  $C_{19}H_{22}O_3$  requires C, 76.5; H, 7.6%). Retention of the ethylenic 11 : 16-double bond was indicated by the ultraviolet light absorption:  $\lambda_{\max}$ , 265 and 300  $\mu$  (log  $\epsilon$  4.57 and 3.84).

The hydroxy-ketone (XIX) (100 mg.) was added in tetrahydrofuran (20 c.c.) at room temperature to lithium aluminium hydride (200 mg.) in tetrahydrofuran (10 c.c.). After 30 min. with occasional shaking the mixture was cooled in ice, decomposed with a solution of sodium potassium tartrate, poured into water, and extracted twice with chloroform. The product, recovered from the combined washed extracts, was crystallised from ethyl acetate, affording cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-1 : 4-dihydroxy-8-methoxychrysenes (XVII), m. p. and mixed m. p. (micro) 179–184°.

The hydroxy-ketone (XIX) (50 mg.) was heated under reflux in ethanol (5 c.c.) with one drop of concentrated hydrochloric acid for 10 min. After cooling, water was added to cloudiness; *trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XIII) separated, having m. p. and mixed m. p. (micro) 177–179°.

The hydroxy-ketone (XIX) suffers partial decomposition to brown material when kept at room temperature in benzene–ethanol solution in the presence of sodium ethoxide, but some (XIX) was recoverable unchanged. Similarly from a boiling solution in 5% ethanolic potassium hydroxide (1 hr.) it (XIX) was largely recovered unchanged.

Catalytic hydrogenation of the hydroxy-ketone (XIX) (200 mg.) in ethanol (70 c.c.) in the presence of 2% palladised strontium carbonate (200 mg.) was rapid and ceased after the uptake of approx. 1 mol. Removal of the catalyst and evaporation gave a mixture of leaflets (A) and prisms (B), which were separated as far as possible by hand-sorting. Recrystallisation of fraction (B) from ethyl acetate afforded prisms, m. p. (micro) 175–191°, not improved by recrystallisation; the ultraviolet light absorption ( $\lambda_{\max}$ , 275  $\mu$ ; log  $\epsilon$  4.16) indicated the presence of a 15 : 16-double bond, and a mixed m. p. with *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XX) (see following paper), m. p. (micro) 192–193°, showed no further extension of the m. p. range. The essential identity of fraction (B) with (XX) was confirmed by their infrared absorption spectra. Fraction (A) on recrystallisation from ethanol–ethyl acetate gave *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysenes (XII) (90 mg.), m. p. and mixed m. p. (micro) 200–208°.

*Catalytic Hydrogenation of cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-Decahydro-8-methoxy-1 : 4-dioxochrysenes (VII). cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-Decahydro-1-hydroxy-8-methoxy-4-oxochrysenes (XXI).*—The diketone (VII) (300 mg.) was hydrogenated in ethyl acetate (30 c.c.) at room temperature and atmospheric pressure in the presence of Adams's platinum oxide catalyst (100 mg.). 1 Mol. of hydrogen was rapidly absorbed and uptake then ceased. The solid residue obtained on removal of the catalyst and evaporation of the solution was

crystallised from ethyl acetate, affording *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1-hydroxy-8-methoxy-4-oxochrysene (XXI), needles (160 mg.), m. p. (micro) 167—168° (Found : C, 76.6; H, 7.5.  $C_{19}H_{23}O_3$  requires C, 76.5; H, 7.4%). Ultraviolet light absorption :  $\lambda_{\max}$ . 272 m $\mu$  (log  $\epsilon$  4.20). Reduction of a sample with lithium aluminium hydride gave *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dihydroxy-8-methoxychrysene (XVI), m. p. and mixed m. p. (micro) 152—156°.

The hydroxy-ketone (XXI) was decomposed by heating it under reflux for 1 hr. with 5% ethanolic potassium hydroxide. It was in part recovered unchanged after being adsorbed on to a column of alkaline alumina overnight and then eluted, the only other material recovered consisting of dark decomposition products.

An attempt was made to effect equilibration with perchloric acid in ethyl acetate. The hydroxy-ketone (XXI) (150 mg.) in alcohol-free ethyl acetate (13 c.c.) was treated with perchloric acid (0.2 c.c. of 72%), and the mixture was kept overnight at room temperature. After dilution with benzene and washing with aqueous sodium hydrogen carbonate the product was recovered, and crystallisation from methanol afforded the *acetate* of (XXI) as needles (70 mg.), m. p. 164—168° (Found : C, 74.4; H, 7.2.  $C_{21}H_{24}O_4$  requires C, 74.2; H, 7.1%). Light absorption : (i) infrared, 1250  $cm^{-1}$  (s) and 1730  $cm^{-1}$  (s) (acetate); (ii) ultraviolet,  $\lambda_{\max}$ . 272 m $\mu$  (log  $\epsilon$  4.20). The substance was identical in m. p., and there was no depression of the m. p. on admixture, with the acetate prepared directly from (XXI) with acetic anhydride-pyridine at room temperature.

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