42. *Studies on the Diels–Alder Reaction. Part V.*[1] *Further Transformation Products of* cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene.*

By P. A. Robins and James Walker.

Equilibration of *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) on alkaline alumina afforded a mixture of the *trans-anti-* (II) and the (?)*trans-syn*-stereoisomer (V), both of which, like (I), were converted into a mixture of *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (VI) and 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (VII; R = Me) by hydrochloric acid in methanol. The *trans-anti*-diketone (II) has been converted into the *trans-anti-cis-* (III) and *trans-anti-trans*-dodecahydro-diketone (IV), and further correlations of stereochemical configuration have been made *via* the $C_{(1)}$-monoketal (IX) of the diketone (I). The formation from compounds having a *trans*-fusion of rings C and D of substances with a *cis*-fusion of these two rings during reactions in which an olefinic double bond migrates from the 11 : 16- to the 15 : 16-position is interpreted in terms of prototropic lability of the products and stereoelectronic kinetic control of ketonisation of derived enols.

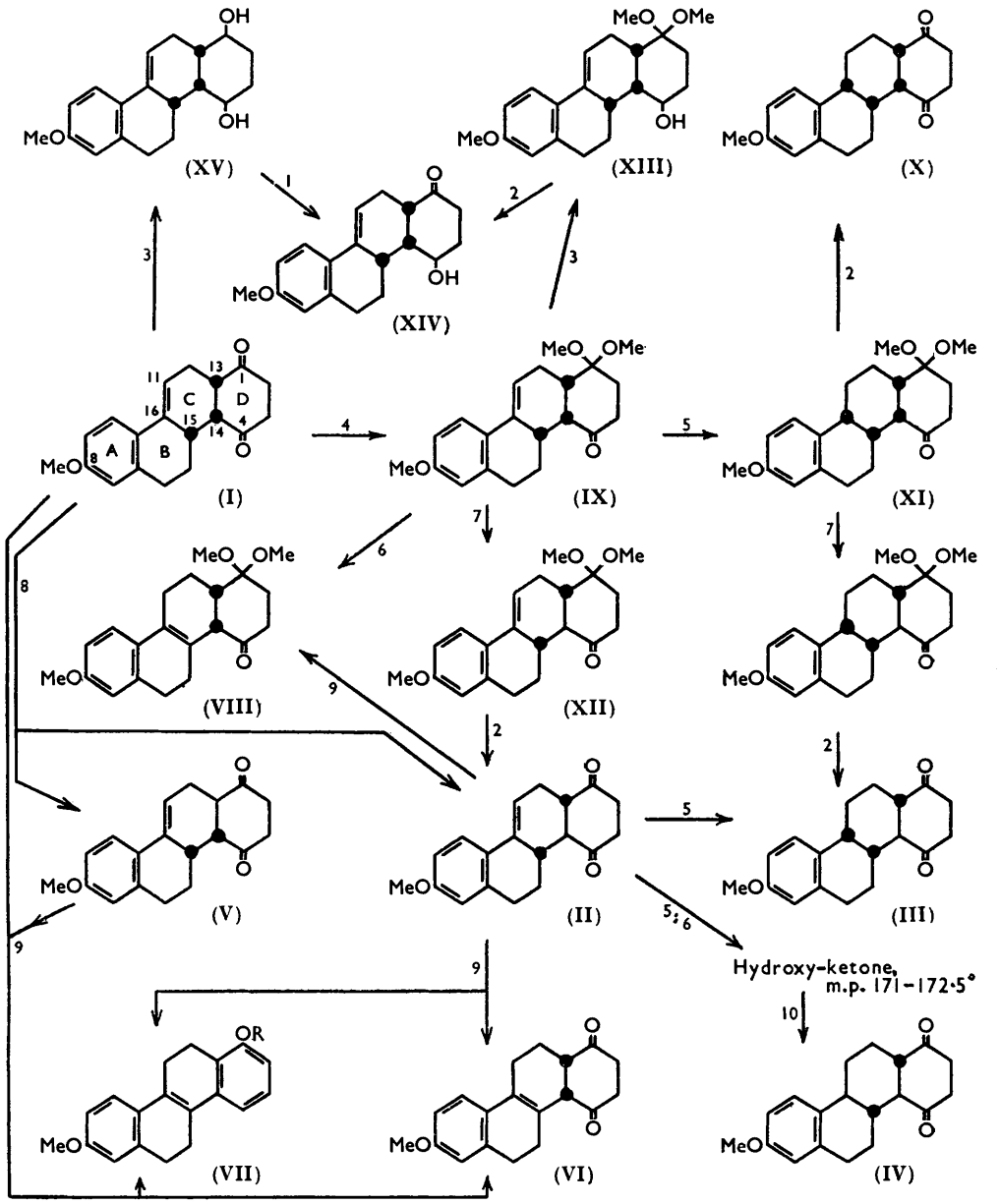
In Part IV[1] the preparation of *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) was described, and a series of transformation products, mostly of the *cis-syn*-configuration, was characterised and interrelated; the ready migration of the 11 : 16-double bond into the 15 : 16-position in the presence of mineral acid was also noted. In the present communication we describe a further series of transformation products derived from the diketone (I), to which access has been gained by stereochemical inversions at points of ring-fusion rendered labile by the presence of adjacent carbonyl groups, effected in such a manner as to permit logical assignment of stereochemical configurations to the resulting products. Starting from the same *cis-syn*-diketone (I) a new and stereoselective total synthesis of œstrone has also been developed and is outlined elsewhere.[2]

On the analogy of experience gained in the hydrophenanthrene series,[3] stereoisomerisation of *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) was effected by passage in benzene solution down a column of alkaline activated alumina. Elution with benzene–chloroform gave a mixture of one major and one minor component, which could be separated by crystallisation. These two products had identical ultraviolet light absorption spectra with maxima at 262 and 294—295 mμ, indicating retention of the olefinic double bond in the 11 : 16-position;[1] these spectra, however, showed significant hypsochromic shifts of the maxima in comparison with those of the starting material (I), and a discussion of these and similar hypsochromic shifts and of their relation to changes in stereochemistry will be incorporated in another communication. That the major component was the expected *trans-anti*-stereoisomer (II) was confirmed by its conversions into *trans-anti-cis-* (III) and *trans-anti-trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (IV), while the minor component was probably the *trans-syn*-stereoisomer (V), which appears on the basis of qualitative conformational analysis to be more stable than the alternative *cis-anti*-form. No chemical evidence for the *trans-syn*-configuration of the minor product could be obtained as insufficient material was available for a detailed study.

Treatment of *trans-anti*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (II) with methanol and hydrochloric acid in a manner similar to that described previously[1] for the *cis-syn*-stereoisomer (I) afforded the *same* products as were

[1] Part IV, Robins and Walker, *J.*, 1956, 3249.
[2] Cole, Johnson, Robins, and Walker, *Proc. Chem. Soc.*, 1958, 114.
[3] Part III, Robins and Walker, *J.*, 1954, 3960.

formed from the latter, namely, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (VI) and 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (VII; R = Me).[1,4] The *same* products, (VI) and (VII; R = Me), were also obtained on similar



Reagents: 1, Oppenauer oxidn. 2, AcOH. 3, $LiAlH_4$. 4, MeOH–AcOH. 5, H_2–Pd. 6, H_2–Pt. 7, OH^-. 8, Al_2O_3. 9, MeOH–HCl. 10, CrO_3.

treatment of the presumed *trans-syn*-stereoisomer (V). When the *trans-anti*-stereoisomer (II) was similarly treated with ethanol and propan-1-ol in the presence of hydrochloric acid the main products isolated were the respective 1-alkoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysenes (VII; R = Et, Pr^n) formed by aromatisation in the manner described in

[4] Robins and Walker, *J.*, 1956, 3260.

recent communications.[4,5] Under the conditions of the ready ketal formation which we have previously described,[4,5] namely, treatment with hot methanol containing a mere trace of hydrogen chloride, the *trans-anti*-diketone (II) afforded the *cis*-ketal, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 1 : 8-trimethoxy-4-oxochrysene (VIII), previously obtained[4] from the *cis-syn*-stereoisomer (I). The formation of compounds with a *cis*-fusion from substances having a *trans*-fusion of rings C and D in these experiments is discussed below.

Catalytic hydrogenation of the *trans-anti*-diketone (II) under neutral conditions with palladium and platinum catalysts gave a more complex (or less readily separable) mixture than that obtained from the corresponding compound in the analogous perhydrophenanthrene series.[3] The main component obtained on hydrogenation interrupted after absorption of 1 mol. of hydrogen was a diketone, m. p. 171—174°, which was separated by crystallisation. This diketone, which is subsequently shown to be *trans-anti-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (III), was unstable to passage in solution down a column of alkaline alumina, giving a mixture which could not be separated by crystallisation; further catalytic hydrogenation also gave a mixture inseparable by crystallisation.

Two further components of the mixture obtained by neutral hydrogenation to completion of the *trans-anti*-diketone (II) were separated by chromatography on alumina. Each was a dodecahydro-hydroxy-ketone, as shown by the presence of both hydroxyl and carbonyl absorption bands in their infrared spectra and anisole-type ultraviolet light absorption spectra. One, m. p. 171—172·5°, on oxidation with chromium trioxide in acetic acid at room temperature gave in poor yield a diketone, m. p. 181—184°, differing from the *trans-anti-cis*-diketone (III) described above. The hydroxy-ketone, m. p. 171—172·5°, which gave a toluene-*p*-sulphonyl derivative under mild conditions, was probably *trans-anti-trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-4-hydroxy-8-methoxy-1-oxochrysene, in analogy with the behaviour observed in the perhydrophenanthrene series,[3] and the diketone obtained from it must have been *trans-anti-trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (IV). The second hydroxy-ketone, m. p. 181—185°, gave no recognisable product on oxidation with chromium trioxide in acetic acid at room temperature, and, on a number of occasions, similar oxidations have failed, possibly owing to attack by the oxidising agent at the highly reactive 6- and 16-carbon atoms. Indeed, in an attempt to hydrogenate the *trans-anti*-diketone (II) in acetic acid with a platinum catalyst and then to re-oxidise the resultant mixture of diols with chromium trioxide in acetic acid, the only product isolated was a small quantity of a compound giving analytical figures suggesting the formula $C_{19}H_{20}O_5$, and showing a strong infrared carbonyl absorption band at 1770 cm.$^{-1}$ besides the expected one at 1710 cm.$^{-1}$, and a hydroxyl absorption band at *ca.* 3380 cm.$^{-1}$.

cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Decahydro-1 : 1 : 8-trimethoxy-4-oxochrysene (IX), the preparation of which by the action of methanol and acetic acid on the corresponding *cis-syn*-diketone (I) is described elsewhere,[2] has been a useful starting-point for providing proof of the configurations assigned to some of the compounds described above. On attempted catalytic hydrogenation of the trimethoxy-ketone (IX) in solution in ethyl acetate in the presence of either palladium or platinum catalysts in various forms absorption of hydrogen ceased before the theoretical volume required for saturation of the double bond had been taken up, and ultraviolet spectrophotometric examination of the crude product indicated the occurrence of double-bond migration to the extent of between 41 and 84%; this was confirmed by the isolation of the isomeric *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 1 : 8-trimethoxy-4-oxochrysene (VIII). When, however, methanol was used as solvent, the starting material (IX) being relatively insoluble, hydrogenation at a supported palladium catalyst was rapid and complete, as was shown by the ultraviolet

[5] Robins and Walker, *J.*, 1957, 177.

light absorption spectrum of the crude product. The product failed to crystallise, but on storage for prolonged periods in contact with methanol or, more rapidly, on treatment with warm acetic acid gave the known [1] *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (X). Equilibration of crude *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-1 : 1 : 8-trimethoxy-4-oxochrysene (XI) with boiling methanolic potassium hydroxide again gave a non-crystalline product, but brief treatment with warm acetic acid afforded the expected crystalline *trans-anti-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (III), identical with, and confirming the stereochemical configuration of, the diketone obtained as described above by hydrogenation of the *trans-anti*-diketone (II); this experiment also confirms the *trans-anti*-configuration of the diketone (II) itself.

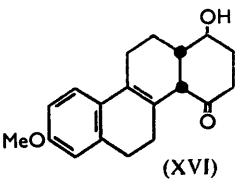
Equilibration of the *cis-syn*-trimethoxy-ketone (IX) itself with boiling alcoholic alkali (or under a variety of other alkaline enolising conditions) gave a mixture, which, from its ultraviolet light absorption spectrum ($\lambda_{max.}$ 264 and 293—298 mμ), must have contained a substantial amount of the *trans-anti*-stereoisomer (XII) of the starting material (IX). Repeated crystallisation of the mixture, however, gave only a small amount of the starting material (IX), and no other pure component could be isolated. After mild treatment with warm acetic acid the resultant mixture of diketones was separated more readily into the relatively insoluble *cis-syn*-diketone (I) and the more soluble *trans-anti*-stereoisomer (II), identical with that obtained above by stereoisomerisation of the *cis-syn*-form (I) with alkaline alumina, this confirmed the assigned *trans-anti*-configuration, since in the experiment just described only the 4-carbonyl group is available to effect stereochemical equilibration by enolisation.

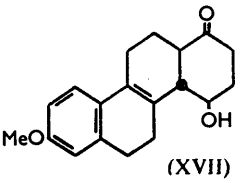
Reduction with lithium aluminium hydride of the *cis-syn*-trimethoxy-ketone (IX) afforded, provided that care was taken in the subsequent working up to prevent hydrolysis of the ketal group or migration of the olefinic double bond, *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-4-hydroxy-1 : 1 : 8-trimethoxychrysene (XIII) which was converted by brief treatment with warm acetic acid into the known [1] *cis-syn*-hydroxy-ketone (XIV); this experiment further identifies conclusively as the compound (XIV) the product of the oxidation [1] by the Oppenauer method of the diol (XV) obtained by reduction of the *cis-syn*-diketone (I) with lithium aluminium hydride. The hydroxy-trimethoxy-compound (XIII) failed to give a toluene-*p*-sulphonyl derivative under mild conditions, and the 4-hydroxyl group is therefore presumably axial, as it was also not attacked in the Oppenauer oxidation, while the 1-hydroxyl group in the diol (XV) is obviously equatorial; these stereochemical relations are precisely analogous to those obtaining in the corresponding compound in the hydrophenanthrene series.[3]

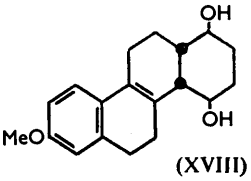
A noteworthy feature of the stereochemical transformations recorded in the present communication is the repeated occurrence of the formation from a compound having a *trans*-fusion of rings C and D of a substance with a *cis*-fusion of these two rings during reactions in which an olefinic double bond migrates from the 11 : 16- into the 15 : 16-position. Thus, the *trans-anti*- (II) and (?)*trans-syn*-diketone (V) having the olefinic double bond in the 11 : 16-position are both converted by suitable treatment with methanolic hydrochloric acid into the *cis*-diketone (VI) with the olefinic double bond in the 15 : 16-position, while ketal formation by the 1-carbonyl group of the *trans-anti*-diketone (II) affords the *cis*-trimethoxy-ketone (VIII). To these observations one may add the fact that *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1-hydroxy-8-methoxy-4-oxochrysene (XVI) is stable to attempted stereoisomerisation with perchloric acid in ethyl acetate (and is largely decomposed by alkaline reagents),[1] but it should be pointed out that an additional factor opposing *cis* ⟶ *trans* conversion in this instance is the need for the equatorial 1-hydroxyl group in the *cis*-form to assume an axial position in the *trans*-stereoisomer. In contrast with these observations is the fact that *cis-syn*-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XIV), although, contrary to expectation, found not to have undergone stereochemical inversion at $C_{(13)}$ during its formation in the Oppenauer

oxidation of the *cis-syn*-diol (XV), passed readily on treatment with alcoholic hydrochloric acid into the *trans*-hydroxy-ketone (XVII), and the same *trans*-hydroxy-ketone (XVII) was formed directly in the Oppenauer oxidation of the *cis*-diol (XVIII).[1]

The apparently anomalous products are therefore seen to have the olefinic double bond in the 15 : 16-position and to have a carbonyl group at $C_{(4)}$. This system (XIX) would be expected to be a highly labile prototropic system with the position of equilibrium [6] entirely

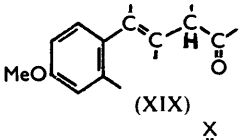

(XVI)


(XVII)

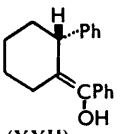

(XVIII)

in favour of the $\Delta^{\beta\gamma}$-form and it should show a strong tendency to enolise, comparable, in fact, with that of ω-styrylacetophenone (XX), which enolises readily and whose enol ketonises rapidly.[7]

We are therefore concerned with the stereochemistry of the ketonisation of the enolic forms (XXI) of compounds (VI), (VIII), and (XVI), and the situation here is analogous to


(XIX)

Ph·CH=CH·CH$_2$·COPh
(XX)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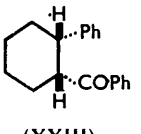
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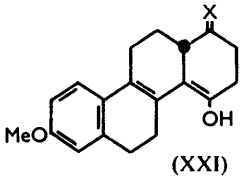
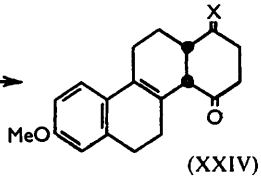

(XXI)


(XXIV)

the cases discussed by Zimmerman,[8] who observed ketonisation of suitably constituted enols to give the thermodynamically less stable form of the related ketone; for example, the enolic form (XXII) of 1-benzoyl-2-phenyl*cyclo*hexane ketonises to give the *cis*-compound (XXIII) with complete stereospecificity. Similar stereoelectronic kinetic control of ketonisation to that operating in Zimmerman's example would favour in the present cases the formation from the enols (XXI) of the thermodynamically less stable *cis*-products (XXIV).

Experimental

M. p.s were observed on a microscope hot stage. Ultraviolet light absorption measurements were made in 96% ethanol. Light petroleum refers to the fraction of boiling range 40—60°, unless otherwise stated. Chromatographic alumina was Type H from Messrs. Peter Spence & Sons, Ltd., unless otherwise stated.

Stereoisomerisation of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (I) *by Alkaline Alumina.—The preparation of* trans-anti- (II) *and* (?)trans-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (V). A solution of the *cis-syn*-diketone (I) (4·0 g.) in benzene (1 l.) was allowed to percolate slowly down a column (internal diam., 4·5 cm.) of alkaline alumina (150 g.); the benzene effluent left no residue on evaporation. Elution with benzene–chloroform (1 : 1) (1·5 l.) gave a pale yellow effluent (A)

[6] Cf. styrylacetic acid (100%) ⇢⇠ γ-phenylcrotonic acid (0%), Bougault, *Compt. rend.*, 1917, **164**, 635; Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell & Sons, Ltd., London, 1953, p. 563.

[7] Wieland and Stenzl, *Ber.*, 1907, **40**, 4825.

[8] Zimmerman, *J. Org. Chem.*, 1955, **20**, 549; Zimmerman and Giallombardo, *J. Amer. Chem. Soc.*, 1956, **78**, 6259.

followed by a brown effluent (B), which was collected separately. Evaporation of the two effluents and crystallisation of the residue from benzene–light petroleum gave trans-anti-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (II) as stout colourless needles (2·42 g.), m. p. 172—174° (Found: C, 76·9; H, 6·9. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%), $\lambda_{max.}$ 262 and 294 mμ (log ε 4·28 and 3·50).

Concentration of the mother-liquors from fraction (A) afforded a mixture of stout needles and rosettes of fine needles which were separated by hand-sorting. Several recrystallisations of the latter from benzene–light petroleum gave the (?)trans-syn-*stereoisomer* (V) as fine needles (0·20 g.), m. p. 174—176°, strongly depressed on admixture with the *trans-anti*-stereoisomer (Found: C, 76·8; H, 6·6%); $\lambda_{max.}$ 262 and 295 mμ (log ε 4·28 and 3·50). The mother-liquors from fraction (B) contained tar which interfered with attempts to isolate the minor component.

Effect of Hydrochloric Acid and Alcohols on trans-anti-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (II).—(a) *Hydrochloric acid and methanol.* The *trans-anti*-diketone (II) (0·5 g.), suspended in boiling methanol (20 c.c.), was treated with concentrated hydrochloric acid (1 c.c.) and heated under reflux for 30 min. After 7 min. a clear yellow solution was obtained. The product (0·48 g.) was recovered crystalline by addition of water, and fractional crystallisation from ethanol afforded *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (VI) (0·22 g.), m. p. 153—156°, and 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (VII; R = Me) (0·15 g.), m. p. 125—127°, identical with specimens obtained previously.[1,4]

(b) *Hydrochloric acid and ethanol.* A similar experiment on a smaller scale employing ethanol and concentrated hydrochloric acid gave as main product 1-ethoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysene (VII; R = Et), m. p. 119—120°, identical with a specimen obtained previously.[1,4]

(c) *Hydrochloric acid and propan*-1-*ol.* Under similar conditions propan-1-ol afforded 5 : 6 : 11 : 12-*tetrahydro*-8-*methoxy*-1-n-*propoxychrysene* (VII; R = Pr^n) which crystallised from propan-1-ol in laths, m. p. 82—82·5° (Found: C, 82·3; H, 7·7. $C_{22}H_{24}O_2$ requires C, 82·5; H, 7·6%), $\lambda_{max.}$ 218, 317, 330, and 346 mμ (log ε 4·28, 4·43, 4·50, and 4·35 respectively).

Effect of Methanolic Hydrogen Chloride on trans-anti-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (II).—The *trans-anti*-diketone (II) (0·2 g.), suspended in boiling methanol (10 c.c.), was treated with saturated methanolic hydrogen chloride (3 drops) and kept at the b. p. for 10 min. On cooling, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 1 : 8-trimethoxy-4-oxochrysene (VIII) (0·13 g.), m. p. 135—138°, separated, identical with a specimen obtained previously.[4]

Effect of Hydrochloric Acid and Methanol on (?)-trans-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (V).—In a similar manner the (?)*trans-syn*-diketone (V) (0·2 g.) in boiling methanol was treated with concentrated hydrochloric acid (1 c.c.) and heated under reflux for 30 min. The product was separated into 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (VII; R = Me), m. p. 124—126°, and *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (VI). The latter was obtained as laths, m. p. 148·5—150°, a new crystalline modification, which was interconvertible with the form previously encountered (plates, m. p. 154—157°); the infrared spectra of the two crystalline forms were almost identical (KCl discs).

Catalytic Hydrogenation of trans-anti-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (II).—The *trans-anti*-diketone (II) (0·1 g.) in ethyl acetate (25 c.c.) was shaken in hydrogen at atmospheric pressure and room temperature in the presence of 2% palladised strontium carbonate (0·1 g.). Absorption of 1 mol. of hydrogen was complete in 2 hr. After recovery in the usual way, recrystallisation of the solid residue from aqueous ethanol afforded trans-anti-cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-*dodecahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (III) as fine needles (50 mg.), m. p. 171—174° (Found: C, 76·3; H, 7·5. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%), $\lambda_{max.}$ 222 (infl.) and 280 mμ (log ε 3·88 and 3·34). The stereochemical configuration was confirmed by an experiment described below and by the instability of the compound to passage in solution down a column of alkaline alumina.

On a larger scale, with ethanol (100 c.c.) as solvent for the *trans-anti*-diketone (II) (1·0 g.), a crystalline precipitate separated after the absorption of slightly more than 1 mol. of hydrogen, and hydrogenation then ceased. Filtration afforded the *trans-anti-cis*-dodecahydro-diketone (III) described above. The material recovered from the filtrate was dissolved in ethyl acetate

(100 c.c.) and hydrogenation was continued in the presence of Adams's platinum oxide catalyst (0·1 g.) until no further absorption took place (total, 2·5 mol.). The residue, left on removal of the catalyst and evaporation of the solvent, was chromatographed on activated alumina (30 g.; Messrs. Savory and Moore Ltd., chromatographic analysis grade). Two main fractions were obtained on elution with benzene and benzene–chloroform (9 : 1) respectively. The first fraction (0·29 g.) on crystallisation from ethyl acetate–light petroleum afforded a *hydroxy-ketone* in the form of plates, m. p. 181—185° (Found: C, 76·2; H, 8·0. $C_{19}H_{24}O_3$ requires C, 76·0; H, 8·1%), $\lambda_{max.}$ 279 mμ (log ε 3·34). The second fraction (0·10 g.) on recrystallisation gave a second *hydroxy-ketone* as needles, m. p. 171—172·5° (Found: C, 76·0; H, 8·1%), having an infrared absorption spectrum markedly different from that of the isomeric substance of m. p. 181—185°. Oxidation of the hydroxy-ketone, m. p. 171—172·5° (60 mg.), in acetic acid (5 c.c.) with chromium trioxide (56 mg., 3 equiv.) at room temperature overnight followed by isolation of the product in chloroform afforded the corresponding *diketone*, crystallising from ethanol in laths, m. p. 181—184° (Found: C, 76·3; H, 7·5. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4%). The infrared spectrum of this diketone differed markedly from that of the *trans-anti-cis*-diketone (III), m. p. 171—174°, described above, and, on analogy with experience in the perhydrophenanthrene series,[3] the diketone, m. p. 181—184°, was doubtless *trans-anti-trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (IV).

The hydroxy-ketone, m. p. 171—172·5°, was recovered unchanged after 1·5 hours' heating under reflux with 5% methanolic potassium hydroxide. On treatment with excess of toluene-*p*-sulphonyl chloride in pyridine at room temperature it afforded a *toluene*-p-*sulphonate*, fine needles (from ethyl acetate–light petroleum), m. p. 174—176° (Found: C, 68·3; H, 6·9. $C_{26}H_{30}O_5S$ requires C, 68·7; H, 6·7%).

Catalytic Hydrogenation of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-1 : 1 : 8-*trimethoxy*-4-*oxochrysene* (IX) *and Transformations of the Products Therefrom.* trans-anti-cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-*Dodecahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (III).—(*a*) Pure trimethoxy-ketone (IX) (0·34 g.) in ethyl acetate (25 c.c.) was hydrogenated at room temperature and atmospheric pressure in presence of Adams's platinum oxide catalyst (50 mg.). Absorption of hydrogen ceased after less than one-third of the calculated requirement, and ultraviolet spectrophotometry indicated that double-bond migration had taken place to the extent of 84% ($\lambda_{max.}$ 274 mμ; log ε 4·13, calc. on *M* 342). Removal of the catalyst and evaporation of the solvent gave a residue, which, on crystallisation from methanol, afforded *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 1 : 8-trimethoxy-4-oxochrysene [4] (VIII), m. p. and mixed m. p. 135—137°.

(*b*) Pure trimethoxy-ketone (IX) (0·5 g.), suspended in methanol (50 c.c.), was hydrogenated at room temperature and atmospheric pressure in the presence of 10% palladised strontium carbonate (1·0 g.). Rapid absorption of the theoretical volume of hydrogen occurred, and filtration of the catalyst and evaporation of the solvent under reduced pressure with the minimum application of heat gave a gum which failed to crystallise ($\lambda_{max.}$ 278 mμ; log ε 3·38, calc. on *M* 344). On prolonged storage in contact with methanol the gum formed massive prisms which proved to be *cis-syn-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene [1] (X), m. p. and mixed m. p. 161—165°.

(*c*) The trimethoxy-ketone (IX) (0·33 g.) in methanol (40 c.c.) was hydrogenated as in (*b*) (above). After removal of the catalyst, potassium hydroxide (0·4 g.) in a few drops of water was added, and the mixture was heated under reflux for 1 hr., cooled, and poured into water containing a slight excess of acetic acid. The product was extracted with chloroform (five times), and the combined extracts were washed successively with water, aqueous sodium hydrogen carbonate solution, and water, then dried and evaporated under reduced pressure with the minimum application of heat, to give a brown gum. On dissolution of this in a small volume of warm acetic acid and addition of water a solid separated. Crystallisation from methanol–ethyl acetate then afforded *trans-anti-cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14 : 15 : 16-dodecahydro-8-methoxy-1 : 4-dioxochrysene (III), m. p. 169—173°, identical in m. p., mixed m. p., and infrared absorption spectrum with the specimen obtained as above by catalytic hydrogenation of *trans-anti*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (II).

Alkaline Equilibration of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-1 : 1 : 8-*trimethoxy*-4-*oxochrysene* (IX).—Freshly purified ketal (IX) (0·50 g.; $\lambda_{max.}$ 265·5 and 300·5 mμ; log ε 4·29 and 3·56) in methanol (50 c.c.) containing potassium hydroxide (2·5 g.) was heated

under reflux for 1 hr. After rapid cooling, water was added to cloudiness; when crystallisation was complete the solid was collected and dried in air [0·47 g.; m. p. 130—150°; $\lambda_{max.}$ 264 and 293—298 (plateau) mμ; log ε 4·31 and 3·56]. Repeated crystallisation from methanol of a portion of the solid gave only a small recovery of starting material, and the other component of the mixture could not be isolated.

A portion of the crude product (0·20 g.) was dissolved by gentle warming in acetic acid (2 c.c.), and water was added after a few minutes. The precipitated yellowish needles (0·14 g.) had m. p. 155—185°, and were separated by repeated crystallisation from methanol into a less soluble fraction (23 mg.), fine needles, m. p. 200—203°, identical with the *cis-syn*-diketone (I), and a more soluble fraction (32 mg.), stout needles, m. p. 175—177°, identical with the *trans-anti*-stereoisomer (II), described above.

Reduction of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-1 : 1 : 8-*trimethoxy*-4-*oxochrysene* (IX) *by Lithium Aluminium Hydride.* cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-4-*hydroxy*-1 : 1 : 8-*trimethoxychrysene* (XIII).—Pure trimethoxy-ketone (IX) [2] (0·5 g.) in dry ether (200 c.c.) was added slowly to a stirred suspension of lithium aluminium hydride (0·5 g.) in ether (100 c.c.) at 0° during 1 hr. After a further ½ hr. the excess of reagent was decomposed by a little saturated aqueous sodium sulphate solution, followed by anhydrous sodium sulphate. The ethereal solution was decanted and evaporated after the addition of a drop of pyridine. Crystallisation of the solid residue from light petroleum (b. p. 60—80°) afforded cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*decahydro*-4-*hydroxy*-1 : 1 : 8-*trimethoxychrysene* (XIII) as needles, m. p. 146—150° (Found: C, 73·5; H, 8·1. $C_{21}H_{28}O_4$ requires C, 73·2; H, 8·2%), $\lambda_{max.}$ 266 and 300 mμ (log ε 4·32 and 3·59 respectively). The compound (XIII) failed to form a toluene-*p*-sulphonate on treatment at room temperature with an excess of toluene-*p*-sulphonyl chloride in pyridine. On dissolution of the substance (XIII) in warm acetic acid, stout needles separated, and recrystallisation from ethyl acetate afforded *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-4-hydroxy-8-methoxy-1-oxochrysene [1] (XIV), m. p. and mixed m. p. 189—192°.

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