633. *A New and Specific Aromatisation Reaction. Part I. Direct
Conversion of* cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro-8-
methoxy-1 : 4-dioxochrysene into* 1-*Alkoxy-5 : 6 : 11 : 12-tetrahydro-8-
methoxychrysenes.*

By P. A. ROBINS and JAMES WALKER.

It is shown that by-products formed during the isomerisation of *cis-syn*-
1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene
(I) into *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-di-
oxochrysene (II) in hot alcohol in the presence of aqueous hydrochloric acid
are 1-alkoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysenes (XIII). The
compositions of these substances correspond to the addition to (II) of the
elements of the alcohol employed and the loss of two molecules of water, and
a mechanism is proposed for this novel aromatisation of a 1 : 4-dioxohexa-
methylene ring to give an alkoxylated benzene ring.

Precise conditions for the preparation of the 1-alkoxy-5 : 6 : 11 : 12-tetra-
hydro-8-methoxychrysenes (XIII) as major products have been established,
and ready ketal formation by the carbonyl group in the 1-position of the *cis*-
diketone (II) has been demonstrated.

IN the preceding communication it was noted that in the conversion of *cis-syn*-
1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) into *cis*-
1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (II) in hot
ethanolic hydrochloric acid there was formed in about 20% yield a by-product $C_{21}H_{22}O_2$,
and in methanolic hydrochloric acid a similar by-product $C_{20}H_{20}O_2$, containing two
methoxyl groups. The ultraviolet light absorptions of these two substances were
virtually indistinguishable and markedly different from those of their precursors, indicating
a radical change in structure. The two methoxyl groups in the latter compound,
$C_{20}H_{20}O_2$, accounted for the two oxygen atoms, and the original two carbonyl groups had
disappeared. The substances were, in fact, apparently derived from the diketone (I) or
(II) by the loss of the elements of two molecules of water and the addition of the elements
of the alcohol employed, and it is the object of the present communication to demonstrate
the structures of these compounds and to propose a mechanism for their formation.

The ultraviolet light absorption spectra of the compounds $C_{20}H_{20}O_2$ and $C_{21}H_{22}O_2$ (Fig. 1) showed intense absorption in the 310—350 mμ region with maxima at 316, 330, and 346 mμ, strongly reminiscent of the spectrum of *trans*-stilbene in which the three maxima

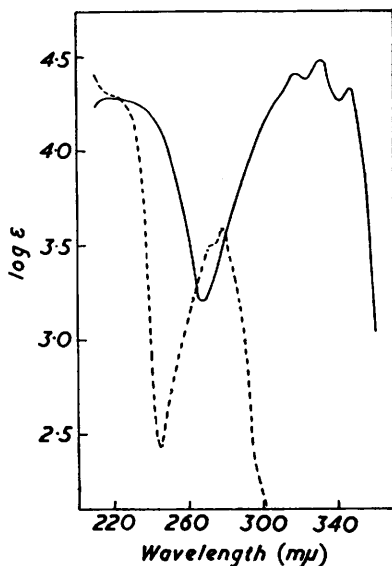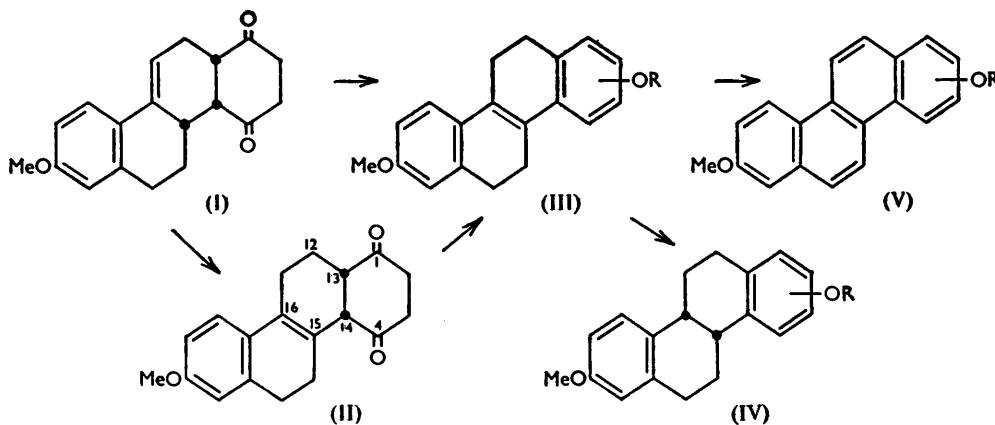Fig. 1.   *Ultraviolet light absorption, in hexane, of 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (III; R = Me) (———), and* cis-5 : 6 : 11 : 12 : 15 : 16-*hexahydro-1 : 8-dimethoxychrysene (IV; R = Me) (– – – –).*

Fig. 2.   *Ultraviolet light absorption of 1 : 8-dimethoxychrysene (V; R = Me) in hexane.*

are each shifted by about 20 mμ to shorter wavelengths,[1] so that structure (III) may therefore be provisionally assigned to the substances $C_{20}H_{20}O_2$ and $C_{21}H_{22}O_2$.   In agreement with this view, catalytic hydrogenation of the two compounds in acetic acid in presence of Adams's platinum oxide catalyst stopped after the absorption of one mol. of hydrogen,


to give two new compounds (IV), having ultraviolet light absorption spectra (Fig. 1) of the anisole type,[2] and indicating that hydrogenation had saturated the olefinic double bond in (III) to give, in each case, a substance (IV) containing two isolated benzenoid chromophores.

[1] Cf. Beale and Roe, *J.*, 1953, 2757.
[2] Cf. Wolf and Herold, *Z. phys. Chem.*, 1931, **13**, *B*, 225.

Furthermore, dehydrogenation of the substance $C_{20}H_{20}O_2$ with chloranil in boiling anisole afforded a substance $C_{20}H_{16}O_2$, containing two methoxyl groups and having an ultraviolet light absorption spectrum (Fig. 2) typical [3] of a fully aromatic chrysene derivative (V). It therefore remained to establish the point of attachment of the alkoxy-group introduced during the novel aromatisation process disclosed by the above observations.

We were aided in consideration of this matter by the fact that a clear yellow colour had rapidly developed in the initial experiment [4] in which the *cis-syn*-diketone (I) had been treated with ethanolic hydrochloric acid; this recalled the halochromic salts formed by substances such as cinnamaldehyde and cinnamyl-ideneacetone, *e.g.*, $[CHPh{:}CH{\cdot}CH{:}CH{\cdot}C^+(OH){\cdot}CH_3]X^-$, and suggested that a halochromic salt might be involved in the conversion of the 1 : 4-dioxohexamethylene ring of (I) into an alkoxylated benzene ring. As the migration of an 11 : 16-double bond into the 15 : 16-position in substances of type (I) takes place with great ease under the influence of acid,[4] it may be assumed that the isomerisation product (II) is the nearer precursor of (III). Obviously only one of the two carbonyl groups in (II) is suitably placed to participate in a conjugated system involving the aromatic nucleus, namely, that in position 1, and creation of such a conjugated system requires the introduction of a second olefinic double bond into (II) in the 13 : 14-position. We therefore propose the following mechanism for the aromatisation of ring D of (II). Addition of a proton to either carbonyl group in (II) can give a carbonium ion (VI) reversibly. The addition of a proton to the 4-carbonyl group, to give the carbonium ion (VIb), is followed by a 1 : 2-hydride shift (VII) and then loss of the hydrogen atom from the 13-position as a proton to give the conjugated system shown in (VIII); in effect this is formally the conversion of a saturated ketone into an αβ-unsaturated alcohol, the reverse of which is already known [5] in the conversion of 3-hydroxy-cholest-4-en-6-one (IX) into cholestane-3 : 6-dione (X). The 1-carbonyl group in (VIII) is now favourably placed for the formation of a halochromic salt (XI), and metathetic replacement of the 1-hydroxyl group by alkoxyl could take place by presentation of a pair of unshared electrons by the oxygen atom of the alcohol to the carbonium carbon atom
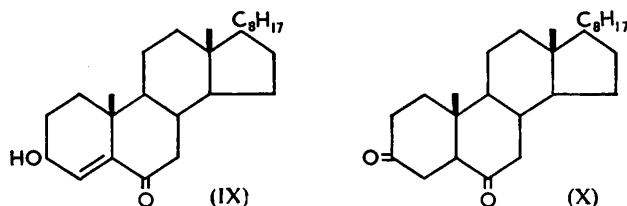
and separation of the elements of water (XII). The next stage—decomposition of the reaction mixture with water—involves the loss (solvation) of a proton from the 2-position in (XII) and further spontaneous loss of the elements of one molecule of water from what would then be a hydroxy-dihydrobenzene derivative to give theoretically the 1-alkoxy-8-methoxychrysene (XIII).

The two compounds $C_{20}H_{20}O_2$ and $C_{21}H_{22}O_2$ should therefore, according to the above mechanism, have been 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (XIII ; R = Me) and 1-ethoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysene (XIII ; R = Et) respectively. and this orientation was confirmed by direct comparison of the dehydrogenation product (V ; R = Me) with a specimen of 1 : 8-dimethoxychrysene (XVIII ; R = Me), obtained by an adaptation of Cook and Schoental's synthesis [6] of 1-hydroxychrysene, as described below. The orientation was further confirmed by establishing the identity of the chloranil dehydrogenation product from (III ; R = CH_2Ph) (see below) with synthetic 1-benzyloxy-8-methoxychrysene (XVIII ; R = CH_2Ph).

[3] Cf. Holiday and Jope, *Spectrochim. Acta*, 1950, **4**, 157.
[4] Robins and Walker, preceding paper.
[5] Heilbron, Jones, and Spring, *J.*, 1937, 801; cf. Butenandt and Schramm, *Ber.*, 1936, **69**, 2289; Butenandt and Hausmann, *Ber.*, 1937, **70**, 1154; Jeanloz, Prins, and von Euw, *Helv. Chim. Acta*, 1947, **30**, 374; Herzig and Ehrenstein, *J. Org. Chem.*, 1951, **16**, 1050.
[6] Cook and Schoental, *J.*, 1945, 288.

The Reformatsky reaction with zinc and methyl γ-bromocrotonate was applied to 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-oxophenanthrene (XIV), prepared by a combination of the methods of Stork [7] and of Ross,[8] and the methyl ester (XV; R = Me) of the resulting γ-(1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-phenanthrylidene)crotonic acid (XV; R = H) was rearranged when heated with palladium black to methyl γ-(7-methoxy-1-phen-anthryl)butyrate (XVI; R = Me). The free acid (XVI; R = H) was cyclised with anhydrous hydrofluoric acid to give 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-oxochrysene (XVII), and dehydrogenation of this with palladium black in boiling α-methylnaphthalene
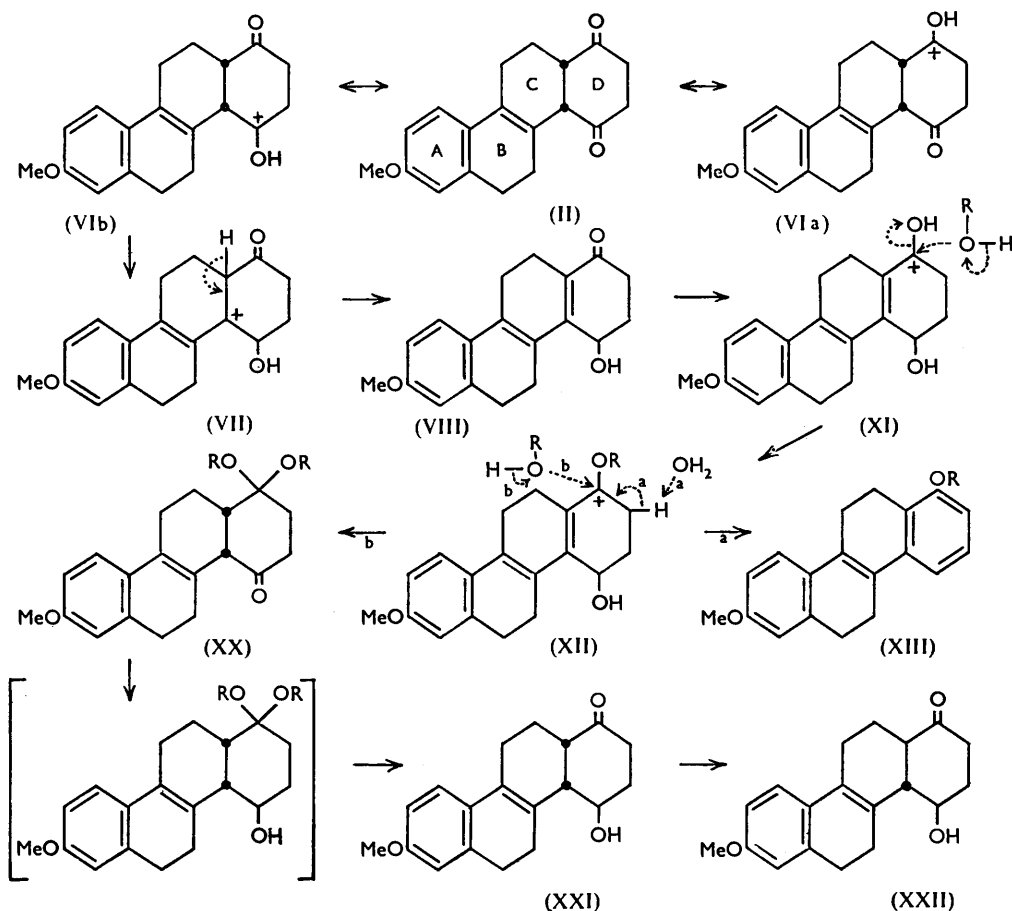

proceeded slowly and incompletely, even after 72 hr., to give 1-hydroxy-8-methoxychrysene (XVIII; R = H). The derived methyl ether (XVIII; R = Me) had m. p. and ultra-violet and infrared light absorption spectra identical with those of the substance (V; R = Me) obtained by chloranil dehydrogenation of the substance $C_{20}H_{20}O_2$ (III; R = Me), as described above. The benzyl ether (XVIII; R = CH$_2$Ph) was obtained by the action of benzyl chloride on (XVIII; R = H) in boiling acetone in the presence of potassium carbonate. Treatment of the ketone (XVII) with methylmagnesium iodide, followed by dehydration of the resulting alcohol and dehydrogenation, afforded 8-methoxy-1-methyl-chrysene (XIX) required as a reference substance in the preceding communication.[4]

Having shown that the above mechanism predicted the orientation of the products

[7] Stork, *J. Amer. Chem. Soc.*, 1947, **69**, 2936.
[8] Ross, *J.*, 1947, 1365.

obtained by the aromatisation of ring D in (I), or (II), in the presence of hydrochloric acid and an alcohol, we then turned to the possibility of establishing conditions whereby the aromatisation products (XIII) might be the major products, and the following general process, which at no stage exceeds room temperature, was found to give excellent results. The 1 : 4-dioxochrysene (I) was dissolved in alcohol-free chloroform, and the solution was saturated with dry hydrogen chloride at 0°; a cherry-red colour and a strong fluorescence developed, owing presumably to formation of the halochromic salt (XI), and subsequent addition of the alcohol did not cause a significant colour change. The mixture, containing the appropriate alcohol, was set aside overnight at room temperature, protected from moisture, some deepening and browning of the colour, but otherwise
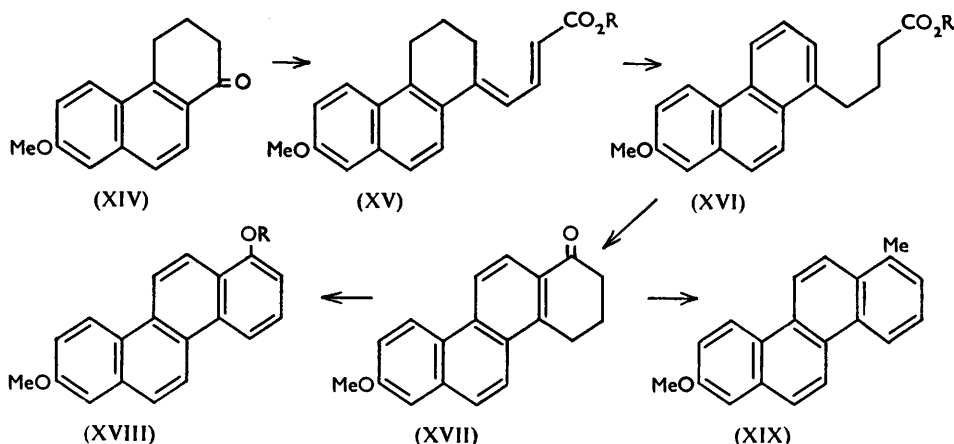
no significant change in appearance, taking place. On addition of water an immediate change in colour to greenish-brown occurred and the chloroform layer became more strongly fluorescent. The products, recovered from the washed chloroform solutions, readily crystallised, and in the case of methanol and ethanol were the previously encountered methyl and ethyl ethers, $C_{20}H_{20}O_2$ and $C_{21}H_{22}O_2$ (XIII; R = Me, Et), which were now obtained in high yield. Benzyl alcohol afforded a new benzyl ether (XIII; R = CH_2Ph), having an ultraviolet light absorption spectrum closely related to those of the corresponding methyl and ethyl analogues with the superimposed absorption of the benzyl group. That the benzyloxy-group was in fact in the 1-position was confirmed by dehydrogenation with chloranil to give 1-benzyloxy-8-methoxychrysene (XVIII; R = CH_2Ph), identical with that prepared by benzylation of authentic 1-hydroxy-8-methoxychrysene (XVIII; R = H) (above). When, however, no alcohol was added to the red chloroformic hydrogen chloride solution of the *cis-syn*-diketone (I) before the final addition of water, the usual working-up procedure gave as sole product the *cis*-diketone (II), which could, of course, itself be utilised as the starting material for the aromatisation, when alcohol was added to its red solution in chloroformic hydrogen chloride. The *cis*-diketone (II) was also the product when acetic acid was added instead of an alcohol to the chloroformic hydrogen chloride solution of (I) before the addition of water. The formation of the *cis*-1 : 4-diketone by reaction of the halochromic salt with water implies, according to our proposed mechanism, reversion of (IX) to (VIII) and reversion of (VIII) to (II), on the analogy of the conversion of (XI) into (X). The formation of the *cis*-diketone (II) is, moreover, in accord with considerations which we have previously advanced [9] concerning the stereochemical stability of fused 1 : 4-dioxo*cyclo*hexane rings.

A further interesting property of the 1-carbonyl group in the *cis*-diketone (II) was the very great ease with which it formed a dimethyl ketal. A few minutes at the boiling point in methanol containing a trace of hydrogen chloride sufficed to convert it in excellent yield

[9] Robins and Walker, *J.*, 1955, 1789; *Chem. and Ind.*, 1955, 772.

into *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 1 : 8-trimethoxy-4-oxochrysene (XX; R = Me), and an extension [(XII) $\xrightarrow{b}$ (XX)] of the preceding mechanism may be advanced to explain this ready ketal-formation at $C_{(1)}$. Proof that the 1-carbonyl group was involved in the ketal-formation was obtained in the following way. Reduction with lithium aluminium hydride and decomposition of the reaction mixture with cold dilute sulphuric acid afforded *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XXI), identical with the substance obtained on migration of the double bond in *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (preceding communication) into the 15 : 16-position. The keto-alcohol (XXI) was converted by alcoholic alkali into *trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XXII), in which the position of the carbonyl group was established (preceding communication) by its conversion *via* the Grignard reaction into 8-methoxy-1-methylchrysene (XIX).

The similarity between the ultraviolet light absorption of the 1-alkoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysenes (XIII) and that of *trans*-stilbene noted above is of some interest, the bathochromic shifts observed in the case of (XIII) being attributable to the alkoxyl groups. The introduction of an α-methyl substituent into *trans*-stilbene produces a hypsochromic shift of *ca.* 25 mμ, and the introduction of a second alkyl group, in the αβ-dialkylstilbenes, produces a further hypsochromic shift of *ca.* 30 mμ, due to steric interference between the alkyl groups and the respective β-situated aryl groups, the intensity of absorption being also diminished.[10] The effect of introducing the two ethano-bridges in (XIII) is therefore to restore the approximate coplanarity of the molecule with restoration of the ultraviolet light absorption spectrum of *trans*-stilbene. Precisely similar effects are seen in passing from diphenyl to 2 : 2′-substituted diphenyls and thence to 2 : 2′-bridged diphenyls (*e.g.*, 9 : 10-dihydrophenanthrene).[11]

EXPERIMENTAL

General details concerning the observation of m. p.s and the measurement of ultraviolet light absorption are given in the preceding paper.

Catalytic Hydrogenation of 1-*Alkoxy*-5 : 6 : 11 : 12-*tetrahydro*-8-*methoxychrysenes* (XIII; R = Me, Et).—The tetrahydrochrysene (XIII; R = Me) (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.). Removal of the catalyst and distillation under reduced pressure gave a solid residue, which, after several crystallisations from benzene–methanol, afforded cis-5 : 6 : 11 : 12 : 15 : 16-*hexahydro*-1 : 8-*dimethoxychrysene* (IV; R = Me) as needles, m. p. (micro) 127—128°, depressed to 90° on admixture with the starting material (XIII; R = Me) (m. p. 125—127°) (Found : C, 81·4; H, 7·5; OMe, 20·9. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5; OMe, 20·7%). Ultraviolet light absorption in hexane : $\lambda_{max.}$ 220 (infl.), 273 (infl.), and 279 mμ (log ε 4·3, 3·50, and 3·60 respectively) (Fig. 1).

Similarly, catalytic hydrogenation of the homologue (XIII; R = Et) gave cis-1-*ethoxy*-5 : 6 : 11 : 12 : 15 : 16-*hexahydro*-8-*methoxychrysene* (IV; R = Et), which crystallised from ethanol in colourless plates, m. p. (micro) 96—98° (Found : C, 81·8; H, 7·8. $C_{21}H_{24}O_2$ requires C, 81·8; H, 7·8%). The ultraviolet light absorption was almost identical with that of the dimethoxy-analogue (above).

Dehydrogenation of 5 : 6 : 11 : 12-*Tetrahydro*-1 : 8-*dimethoxychrysene* (XIII; R = Me). 1 : 8-*Dimethoxychrysene* (XVIII; R = Me).—The tetrahydrochrysene (XIII; R = Me) (200 mg.) was heated in anisole (25 c.c.) under reflux with chloranil (510 mg., 3 equiv.) for 6 hr. After cooling and dilution with benzene, the solution was washed twice with aqueous alkaline sodium dithionite, then with water, and evaporated under reduced pressure. The solid residue was recrystallised from benzene–methanol to give 1 : 8-dimethoxychrysene (XVIII; R = Me) (130 mg.) as plates, m. p. (micro) 190—200° (transition to liquid crystals) and 203—205°, identical in behaviour with, and on admixture with, the synthetic material described

[10] Wessely, Bauer, Chwala, Plaichinger, and Schönbeck, *Monatsh.*, 1948, **74**, 596; Braude, *J.*, 1949, 1902.
[11] Cf. Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

below (Found : C, 83·5; H, 5·6; OMe, 20·8. Calc. for $C_{20}H_{16}O_2$: C, 83·3; H, 5·6; OMe, 20·5%). Ultraviolet light absorption in hexane : $\lambda_{max.}$ 231, 265 (infl.), 274, 310, 327, 348, and 366 mμ (log ε 4·47, 4·81, 4·91, 4·24, 4·01, 3·40, and 3·24 respectively) (Fig. 2). Johnson *et al.*[12] record m. p. 198—200·5°.

γ-(1 : 2 : 3 : 4-*Tetrahydro-7-methoxy-1-phenanthrylidene*)*crotonic Acid* (XV; R = H).—Zinc needles (4·5 g.) were heated in benzene (20 c.c.) under reflux with a little dry mercuric chloride for 15 min. After slight cooling, 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-oxophenanthrene[7,8] (XIV) (5·0 g.) and methyl γ-bromocrotonate (6·5 g.) were added, and stirring was started. A vigorous reaction ensued and continued for 5 min., after which the mixture was heated under reflux for 30 min. After slight cooling, zinc (2·0 g.) and methyl γ-bromocrotonate (3·0 g.) were added in benzene (10 c.c.), and heating was continued for 30 min. This addition was repeated twice more at 30 min. intervals, and the whole mixture was heated for a final 30 min., cooled in ice, and decomposed with ice and dilute sulphuric acid. The product was recovered in ether, and the extract was thoroughly washed and dried, and volatile material was removed by distillation on the steam-bath under reduced pressure. The viscous residue (10·4 g.) could with difficulty be induced to crystallise, to give the required methyl ester (XV; R = Me), but it was best hydrolysed directly, and it was therefore heated under reflux in benzene (50 c.c.) and methanol (100 c.c.) with potassium hydroxide (10 g.) for 1 hr. After cooling, the cream-coloured precipitated potassium salt was collected, washed with benzene, and dried (1·92 g.; A). Filtrate and washings were poured into water, and the whole was again filtered to yield a second crop of precipitated potassium salt (1·86 g.; B). The benzene layer of the filtrate was rejected and the aqueous phase was aerated to remove dissolved solvent, and acidified with hydrochloric acid, yielding a resinous brown precipitate (2·53 g.; C), which was collected and dried.

Precipitates A and B were dissolved in hot glacial acetic acid, and, on cooling, γ-(1 : 2 : 3 : 4-*tetrahydro-7-methoxy-1-phenanthrylidene*)*crotonic acid* (XV; R = H) separated as yellow leaflets, m. p. 235—239° (decomp.) (Found : C, 77·2; H, 6·2. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%). Ultraviolet light absorption : $\lambda_{max.}$ 298 and 353 mμ (log ε 4·20 and 4·54). A further quantity (0·77 g.) of less pure acid was obtained by crystallisation of the precipitate C from acetic acid.

Esterification of the acid, suspended in methanol–ether, with a slight excess of ethereal diazomethane gave the *methyl ester* (XV; R = Me), which crystallised from ligroin in yellow plates, m. p. 131—133° (Found : C, 78·0; H, 6·6. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5%).

γ-(7-*Methoxy-1-phenanthryl*)*butyric Acid* (XVI; R = H).—The foregoing methyl ester (XV; R = Me) (200 mg.) was heated with palladium black (20 mg.) to 250—270° for 3 hr. in carbon dioxide. On cooling, the product solidified, and solution in hot ligroin and filtration afforded the *butyrate* (XVI; R = Me) as needles, m. p. 119° (Found : C, 78·1; H, 6·7. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5%).

On a larger scale [2·15 g. of (XV; R = Me)], the rearranged methyl ester (XVI; R = Me) was hydrolysed directly after being heated with palladium (200 mg.). It was dissolved in hot benzene (50 c.c.) and poured into 10% methanolic potassium hydroxide (100 c.c.), and the whole was heated under reflux for 1·5 hr., cooled, and poured into much water. The aqueous phase, after a further extraction with benzene, was freed from traces of benzene by aeration, filtered to remove suspended palladium black, and acidified. The precipitated acid (1·8 g.) crystallised from hot glacial acetic acid, to give γ-(7-*methoxy-1-phenanthryl*)*butyric acid* (XVI; R = H) as colourless leaflets, m. p. 176—177° (Found : C, 77·3; H, 6·1. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%).

1 : 2 : 3 : 4-*Tetrahydro-8-methoxy-1-oxochrysene* (XVII).—The preceding acid (2·38 g.) was added to anhydrous hydrogen fluoride (20 c.c.) contained in an ice-cooled Polythene bottle. After 2 hr. in ice the hydrogen fluoride was evaporated and aqueous sodium carbonate was added to the solid residue, followed by chloroform to dissolve the insoluble part. The chloroform layer was separated, washed with water, and evaporated, to give a solid residue, affording, on crystallisation from benzene–light petroleum, 1 : 2 : 3 : 4-*tetrahydro-8-methoxy-1-oxochrysene* as leaflets (1·95 g.), m. p. 225—229° (Found : C, 82·5; H, 6·0. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%). Ultraviolet light absorption : $\lambda_{max.}$ 253 (infl.), 271, 280, 295 (infl.), 322 (log ε 4·17, 4·75, 4·87, 4·37, 4·27).

1-*Hydroxy-8-methoxychrysene* (XVIII; R = H).—1 : 2 : 3 : 4-Tetrahydro-8-methoxy-1-oxo-chrysene (0·5 g.) was heated with palladium black (90 mg.) in boiling α-methylnaphthalene (20 c.c.) in dry oxygen-free nitrogen for 24 hr. After filtration of the hot solution, cooling afforded

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[12] Johnson, Banerjee, Schneider, Gutsche, Shelberg, and Chinn, *J. Amer. Chem. Soc.*, 1952, **74**, 2832.

leaflets (0·33 g.) of 1-*hydroxy*-8-*methoxychrysene* which, crystallised from butan-1-ol or ethyl methyl ketone, had m. p. 244—246° (sealed evacuated capillary), and rapidly became brown on exposure to light and air; both recrystallised samples and specimens sublimed at 210°/0·005 mm. gave low carbon figures on combustion (Found : OMe, 11·5. $C_{19}H_{14}O_2$ requires OMe, 11·3%). Ultraviolet light absorption : $\lambda_{max.}$ 225, 275, and 312 mμ (log ε 4·34, 4·78, and 4·20).

Johnson *et al.*[12] record m. p. 267·8—271° but no analysis for what was " probably " 1-hydroxy-8-methoxychrysene (XVIII; R = H). We have also prepared it, m. p. 254—258° (decomp.), by hydrogenolysis of 1-benzyloxy-8-methoxychrysene(XVIII; R = CH_2Ph), but the same difficulty was encountered in obtaining satisfactory analyses; there were also differences observed in the infrared absorption spectra of the specimens obtained as above and from (XVIII; R = CH_2Ph).

Prolonged reaction with sodium methoxide and excess of methyl iodide in boiling methanol was required to effect methylation of this substance to give 1 : 8-dimethoxychrysene (XVIII; R = Me), crystallising from benzene–methanol in leaflets, m. p. (micro) *ca.* 190° (transition to liquid crystals) and 200—205°, identical with the substance obtained by dehydrogenation of 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (XIII; R = Me); ultraviolet and infrared absorption spectra confirmed the identity.

1-*Benzyloxy*-8-*methoxychrysene* (XVIII; R = CH_2Ph) was obtained from 1-hydroxy-8-methoxychrysene (100 mg.), which was heated under reflux in dry acetone (25 c.c.) with anhydrous potassium carbonate (4 g.) and benzyl chloride (1 c.c.) for 18 hr., two further portions of benzyl chloride (1 c.c.) being added at intervals. After addition of water and benzene, the product was isolated from the organic phase by evaporation of the benzene and excess of benzyl chloride under reduced pressure and sublimation of the residue at 200—220°/0·4 mm. The sublimate crystallised from benzene–methanol to give (XVIII; R = CH_2Ph) as leaflets, m. p. (micro) 158—161° (Found : C, 85·6; H, 5·4. $C_{26}H_{20}O_2$ requires C, 85·7; H, 5·6%).

8-*Methoxy*-1-*methylchrysene* (XIX).—A warm benzene solution of 1 : 2 : 3 : 4-tetrahydro-8-methoxy-1-oxochrysene (XVII) (0·5 g.) was added to methylmagnesium iodide (from 1 g. of magnesium) in boiling benzene. After 1 hour's heating under reflux the mixture was cooled in ice and decomposed with cold 3N-sulphuric acid. The organic layer was separated and washed and the product was recovered in the usual way as a solid (0·42 g.), which from its behaviour on recrystallisation, extended m. p., and analytical figures had probably undergone partial dehydration. The crude material (200 mg.) was heated under reflux in α-methylnaphthalene (20 c.c.) with palladium black (100 mg.) in dry, oxygen-free nitrogen for 20 hr. After cooling and removal of the palladium black, the solvent was distilled under reduced pressure and the residue crystallised from benzene, to give 8-*methoxy*-1-*methylchrysene* as leaflets (150 mg.), m. p. (micro) from 190° (transition to liquid crystals) and 262—263° (Found : C, 88·6; H, 6·3. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9%). Ultraviolet light absorption in hexane : $\lambda_{max.}$ *ca.* 227, 266, 274, 297, 309, and 323 mμ (log ε 4·46, 4·84, 5·08, 4·22, 4·15, and 4·06).

Improved Preparations of 1-*Alkoxy*-5 : 6 : 11 : 12-*tetrahydro*-8-*methoxychrysenes* (XIII) *and of* cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*Decahydro*-8-*methoxy*-1 : 4-*dioxochrysene* (II).—(*a*) A solution of cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) (0·5 g.) in alcohol-free chloroform (20 c.c.) was cooled in ice and saturated with dry hydrogen chloride. The resultant cherry-red solution was allowed to warm to room temperature and methanol (1 c.c.) was added. After being left at room temperature overnight protected from moisture, the red solution was poured into water; the colour changed to greenish-yellow with a pronounced blue fluorescence. The chloroform layer was separated, washed, dried, and evaporated under reduced pressure with gentle warming only. The residue crystallised from benzene–methanol, to give 5 : 6 : 11 : 12-tetrahydro-1 : 8-dimethoxychrysene (XIII; R = Me) (0·39 g.), m. p. (micro) 124—127°, identical with the substance described in the preceding paper.

(*b*) Substitution of ethanol (1 c.c.) for methanol in (*a*) (above) gave 1-ethoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysene (XIII; R = Et) (0·37 g.), m. p. (micro) 119—120°, identical with the substance obtained previously.

(*c*) Substitution of benzyl alcohol (1 c.c.) for methanol in (*a*) (above) afforded 1-*benzyloxy*-5 : 6 : 11 : 12-*tetrahydro*-4-*methoxychrysene* (XIII; R = CH_2Ph) (0·45 g.), m. p. (micro) 123—126°, separating as rods from benzene–methanol (Found : C, 84·9; H, 6·5. $C_{26}H_{24}O_2$ requires C, 84·8; H, 6·6%). Ultraviolet light absorption in hexane : $\lambda_{max.}$ 246 (infl.), 257, 270, 306 (infl.), 318, 332, and 348 (log ε 4·05, 3·77, 3·34, 4·23, 4·41, 4·50, and 4·33). Proof of the orientation of this substance was afforded by dehydrogenation with chloranil (3 equiv.) in boiling anisole for 6 hr., as described above in the case of the 1-methoxy-analogue (XIII; R = Me), to give 1-benzyloxy-8-methoxychrysene (XVIII; R = CH_2Ph), m. p. (micro) 159—161°,

identical with the compound prepared as above by benzylation of 1-hydroxy-8-methoxychrysene (XVIII; R = H).

(*d*) Substitution of glacial acetic acid (1 c.c.) for methanol in (*a*), and otherwise following the same procedure, gave *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (II) (0·43 g.), identical with specimens prepared alternatively. This $\Delta^{15 : 16}$-diketone (II), when subjected to the treatment described in (*a*) (above), again gave 5 : 6 : 11 : 12-tetra-hydro-1 : 8-dimethoxychrysene (XIII; R = Me).

(*e*) Omitting any added reagent after the saturation with hydrogen chloride, but otherwise following the procedure outlined in (*a*) (above), again gave *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (II) (0·37 g.).

cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*Decahydro*-1 : 1 : 8-*trimethoxy*-4-*oxochrysene* (XX; R = Me).—*cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-Decahydro-8-methoxy-1 : 4-dioxochrysene (II) (200 mg.) was dissolved in a few c.c. of boiling methanol with the aid of a few drops of benzene. To the boiling solution were added two drops of a saturated solution of hydrogen chloride in methanol, and the mixture was kept at the b. p. for 5 min., during which some concentration of the solution took place. On cooling, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*decahydro*-1 : 1 : 8-*trimethoxy*-4-*oxochrysene* (180 mg.) separated as pale yellow plates, m. p. 134—138°, not changed on recrystallisation from methanol in the absence of acid; the compound was also recovered unchanged on recrystallisation from aqueous ethanol (Found : C, 73·6; H, 7·6; OMe, 27·1. $C_{21}H_{26}O_4$ requires C, 73·7; H, 7·7; 3OMe, 27·2%). The same result was obtained when *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) was subjected to the same reaction conditions.

Reduction of cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*Decahydro*-1 : 1 : 8-*trimethoxy*-4-*oxochrysene* (XX; R = Me) *with Lithium Aluminium Hydride.* cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*Decahydro*-4-*hydroxy*-8-*methoxy*-1-*oxochrysene* (XXI).—The above ketal (300 mg.) in tetrahydrofuran (15 c.c.) was added to lithium aluminium hydride (200 mg.) in tetrahydrofuran (10 c.c.), and the whole was heated under reflux for $\frac{1}{2}$ hr. After cooling, the mixture was decomposed by ice and dilute sulphuric acid. The product was recovered in chloroform and evaporation gave a solid residue, crystallising from ethyl acetate–light petroleum to give *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*decahydro*-4-*hydroxy*-8-*methoxy*-1-*oxochrysene* (XXI) as colourless plates (210 mg.), m. p. (micro) 192—193° (Found : C, 76·4; H, 7·8. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·6%). Ultraviolet light absorption : $\lambda_{max.}$ 274 mμ (log ε 4·14). This substance was mentioned but not characterised in the preceding communication; its structure was established by the two following experiments.

(*a*) The above hydroxy-ketone (XXI) (100 mg.) in tetrahydrofuran (15 c.c.) was added to lithium aluminium hydride (100 mg.) in tetrahydrofuran (10 c.c.), and the mixture was heated under reflux for $\frac{1}{2}$ hr. The working-up procedure outlined immediately above afforded *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dihydroxy-8-methoxychrysene (60 mg.), m. p. (micro) 152—156°, identical with a specimen prepared by an alternative route (preceding paper).

(*b*) The hydroxy-ketone (XXI) (100 mg.) was heated under reflux with 5% ethanolic potassium hydroxide (20 c.c.) for $\frac{1}{2}$ hr. After cooling and dilution with much water, the product was isolated with the aid of chloroform in the usual manner. Crystallisation from ethyl acetate–light petroleum gave *trans*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-4-hydroxy-8-methoxy-1-oxochrysene (XXII) (60 mg.), m. p. (micro) 174—175°, not depressed on admixture with a specimen prepared by an alternative route (see preceding paper).

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