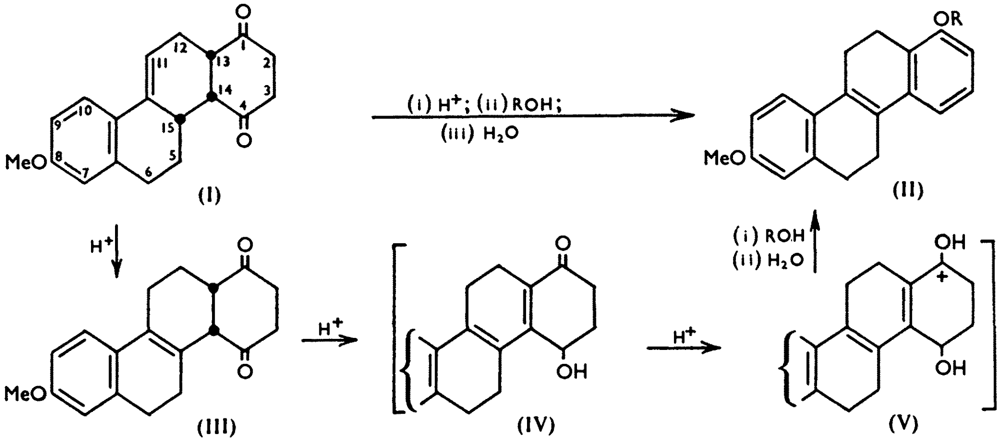
31. *A New and Specific Aromatisation Reaction. Part II.*[1] *Some Further Examples.*

By P. A. Robins and James Walker.

The reaction described in Part I,[1] in which aromatisation of the 1 : 4-dioxo*cyclo*hexane ring in *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) occurred under the influence of hydrogen chloride and alcohols with the formation of 1-alkoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysenes (II), has been shown to be applicable to *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene (VI) and its *p*-methoxy-derivative (VII), *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-1 : 4-dioxochrysene (VIII), and *cis-syn*-1 : 2 : 3 : 10 : 1′ : 2′ : 3′ : 4′-octahydro-1′ : 4′-dioxo-1 : 2-benzofluorene (IX), but only to the extent of about 20% with (VI). Further examples of ready ketal-formation are described.

In the previous communication [1] we described a novel reaction, in which aromatisation of the 1 : 4-dioxo*cyclo*hexane ring in *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) occurred under the influence of hydrogen chloride and alcohols with the formation of 1-alkoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysenes (II). A mechanism was proposed for this reaction involving the migration of the ethylenic double bond from the 11 : 16-position in (I) to the 15 : 16-position (III), followed by an isomerisation introducing a further double bond (IV) and formation of a halochromic salt (V). According to this mechanism certain specific structural conditions must be fulfilled for the aromatisation reaction to take place, prime requirements being (i) that there should be an aromatic nucleus so situated in relation to one of the carbonyl groups of the 1 : 4-dioxo*cyclo*hexane ring as to permit the participation of that carbonyl group in a conjugated system with the aromatic nucleus, so that a halochromic salt may be formed, and (ii) that the carbonyl group not participating in the halochromic salt formation should be converted into a form facilitating the elimination of the oxygen atom in the form of water. In the above mechanism the latter requirement is met by postulating the conversion of the saturated ketone grouping (as in III) into the αβ-unsaturated alcohol group (as in IV), and the double bond so introduced forms part of the conjugated carbonyl system concerned in the formation of the halochromic salt (V). In the present communication four further compounds are discussed in which these structural requirements are



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[1] Part I, Robins and Walker, *J.*, 1956, 3260.

potentially capable of being met. They are *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene (VI) and its *p*-methoxy-derivative (VII), *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-1 : 4-dioxochrysene (VIII), and *cis-syn*-1 : 2 : 3 : 10 : 1′ : 2′ : 3′ : 4′-octahydro-1′ : 4′-dioxo-1 : 2-benzofluorene (IX). In each case aromatisation of the dioxo*cyclo*hexane ring was found to take place under the conditions previously described.[1]

The substances (VI)—(IX) were accessible by condensation of suitable dienes and *p*-benzoquinone, followed by partial reduction of the resulting adducts. 2-Phenylbutadiene has been prepared in low yield by using diverse Grignard reagents,[2] and in more satisfactory yield by pyrolysis of 4-acetoxy-2-phenylbut-1-ene,[3] obtained from α-methylstyrene, formaldehyde, and acetic acid. As we had previously employed acetylene reactions successfully for the preparation of conjugated dienes,[4] we attempted to prepare 2-phenylbutadiene from the acetylenic carbinol derived from acetophenone. Previous workers [5] have obtained indifferent yields in reactions between acetophenone and sodium or lithium acetylide or ethynylmagnesium bromide, but we have found that acetophenone and lithium acetylide in liquid ammonia at room temperature in the presence of a large excess of acetylene [cf. 4b, 6] gave good yields of 2-phenylbut-3-yn-2-ol, which was readily reduced to 2-phenylbut-3-en-2-ol by using Lindlar's lead-poisoned palladium catalyst.[7] Methods for the dehydration of the vinylcarbinol involving acidic reagents gave only polymeric material, although Nazarov and Kotlyarevsky [5d] claim to have used potassium hydrogen sulphate successfully, and in this case Hibbert's method,[8] using iodine, also failed to effect dehydration. Recourse to the method of Price *et al.*[3] was therefore necessary for the preparation of 2-phenylbutadiene. It reacted readily with *p*-benzoquinone in methanol solution, to give *cis*-1 : 4 : 5 : 8 : 9 : 10-hexahydro-1 : 4-dioxo-6-phenylnaphthalene, which was smoothly reduced with zinc and acetic acid at room temperature to *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene (VI). In view of our failure to obtain 2-phenylbutadiene by way of acetylenic precursors, our first attempt to prepare the *p*-methoxyphenyl analogue was made *via* the pyrolytic method. Unfortunately the required 4-acetoxy-2-*p*-methoxyphenylbut-1-ene could not be obtained from *p*-methoxy-α-methylstyrene as the latter polymerised under the conditions used for the Prins reaction, and it was then found that acetylenic intermediates could be used successfully. *p*-Methoxyacetophenone reacted with lithium acetylide in liquid ammonia at room temperature to give an excellent yield of the ethynylcarbinol, which was selectively hydrogenated by using the Lindlar catalyst.[7] Dehydration of the resulting vinylcarbinol took place slowly by the Hibbert procedure,[8] and it may be noted that, in this instance, Nazarov and Kotlyarevsky [5d] report failure using potassium hydrogen sulphate. Without isolation, the intermediate 2-*p*-methoxyphenylbutadiene was allowed to react with *p*-benzoquinone to give *cis*-1 : 4 : 5 : 8 : 9 : 10-hexahydro-6-*p*-methoxyphenyl-1 : 4-dioxonaphthalene, which was then reduced with zinc and acetic acid at room temperature to the desired *cis*-octahydro-compound (VII). In similar fashion, 1-tetralone and 1-indanone were converted *via* the acetylenic and ethylenic alcohols into the dienes, which, without isolation, were allowed to react with *p*-benzoquinone to give *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-1 : 4-dioxochrysene and *cis-syn*-1 : 2 : 3 : 10 : 1′ : 4′-hexahydro-1′ : 4′-dioxo-1 : 2-benzofluorene, and these were reduced with zinc and acetic acid at room temperature to the *cis-syn*-decahydro- (VIII) and *cis-syn*-octahydro-derivative (IX) respectively.

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[2] Carothers and Berchet, *J. Amer. Chem. Soc.*, 1933, **55**, 2813; Backer and Strating, *Rec. Trav. chim.*, 1934, **53**, 525; Alder and Haydn, *Annalen*, 1950, **570**, 201.

[3] Price, Benton, and Schmidle, *J. Amer. Chem. Soc.*, 1949, **71**, 2860.

[4] Robins and Walker, (*a*) *J.*, 1952, 642, 1610; (*b*) *J.*, 1956, 3249.

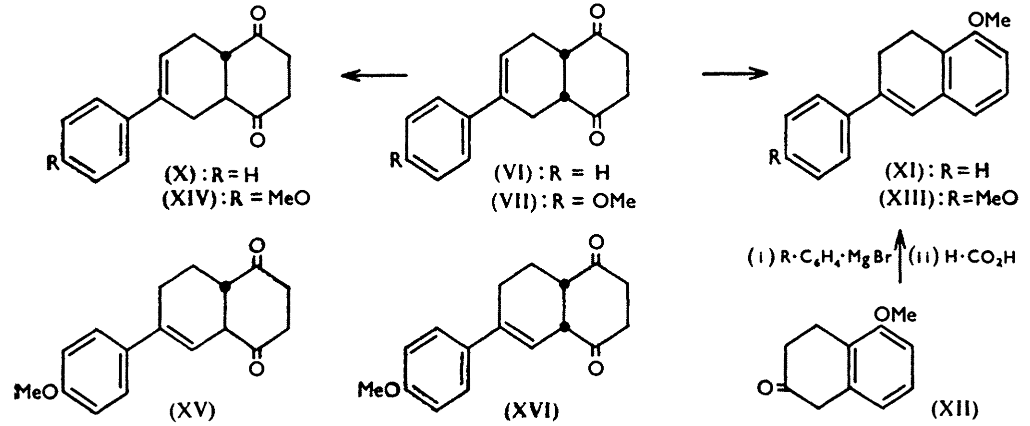
[5] (*a*) Salkind and Rosenfeld, *Ber.*, 1924, **57**, 1690; (*b*) Rupe and Giesler, *Helv. Chim. Acta*, 1928, **11**, 656; (*c*) Oroshnik and Mebane, *J. Amer. Chem. Soc.*, 1949, **71**, 2062; (*d*) Nazarov and Kotlyarevsky, *Bull. Acad. Sci. U.S.S.R.* (*Sect. Chem. Sci.*), 1953, 1100.

[6] Goldberg and Scott, U.S.P. 2,524,787.

[7] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

[8] Hibbert, *J. Amer. Chem. Soc.*, 1915, **37**, 1748.

When an alcohol-free chloroform solution of *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene (VI) was saturated with dry hydrogen chloride at 0°, little colour change, such as is characteristic of halochromic salt formation, was observed, nor was any significant change observed on addition of methanol. When the reaction mixture was worked up the product crystallised, and recrystallisation afforded a compound, m. p. 145—148°, isomeric with the starting material and having an identical ultraviolet light absorption spectrum. The same substance was obtained by allowing the starting material (VI) in benzene solution to percolate through a column of alkaline alumina, conditions which have been found not to cause a shift in the position of the double bond when applied to *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I).[9] The substance of m. p. 145—148° is therefore most probably *trans*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene (X). The mother-liquors from the crystallisation of this compound (X) showed a strong blue fluorescence in ultraviolet light, and chromatography in benzene–light petroleum on alumina afforded a readily eluted colourless fluorescent oil, which solidified and gave, on recrystallisation, 7 : 8-dihydro-1-methoxy-6-phenylnaphthalene (XI), identical in m. p., mixed m. p., and light absorption with an authentic specimen obtained by treatment of 5-methoxy-2-tetralone (XII) with phenylmagnesium bromide and dehydration of the product. In this case, the simplest so far investigated, the aromatisation proceeded to an extent of about 20% only, and this low yield, in comparison with that previously observed [1] and others noted in the present communication, may be due to inherent lack of mobility of the 6 : 7-double bond in (VI) rendering difficult the creation of a conjugated system necessary for halochromic salt formation. Attempts to increase the extent of the conversion of (VI) into (XI) by the use of hydrogen bromide in place of hydrogen chloride were ineffective, and conversion of (X) into (XI) proceeded only to a small extent. The 7 : 8-dihydro-1-methoxy-6-phenylnaphthalene (XI) was readily dehydrogenated by chloranil in boiling anisole to 1-methoxy-6-phenylnaphthalene.



(X) : R = H
(XIV) : R = MeO

(VI) : R = H
(VII) : R = OMe

(XI) : R = H
(XIII) : R = MeO

(XV)

(XVI)

(XII)

In contrast, a solution of *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-6-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (VII) in alcohol-free chloroform developed a clear red colour on saturation with dry hydrogen chloride at 0°, the colour deepening and becoming brownish on subsequent addition of methanol. Isolation of the product gave 7 : 8-dihydro-1-methoxy-6-*p*-methoxyphenylnaphthalene (XIII) in high yield, and no other substance could be isolated. The dihydronaphthalene (XIII), showing typical *trans*-stilbene-like ultraviolet light absorption in the 300—320 mμ region (Fig. 1), was identical with an authentic specimen, obtained by treatment of 5-methoxy-2-tetralone (XII) with *p*-methoxyphenylmagnesium bromide and dehydration of the resulting alcohol.

[9] Unpublished observation.

Dehydrogenation with chloranil in boiling anisole gave 1-methoxy-6-*p*-methoxyphenylnaphthalene. When the addition of methanol was omitted from the preceding experiment, a ketonic product, m. p. 171—172°, isomeric with the starting material, was obtained, and the same substance was obtained when a benzene–light petroleum solution of the *cis*-diketone (VII) was allowed to percolate through a column of alkaline alumina. On the basis of the analogous case [9] cited above, the latter treatment was not expected to cause a shift in the position of the ethylenic double bond in (VII) and a probable structure for the substance of m. p. 171—172° would have been *trans*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-6-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (XIV). On the other hand, the readiness with which colour developed and the extent to which aromatisation of the dioxo*cyclo*hexane ring of (VII) took place in the preceding experiment to give a product with the ethylenic double bond in the 5 : 6-position suggest that the compound, m. p. 171—172°, also contains a double bond in the 5 : 6-position, and that it is either *trans*-(XV) or *cis*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-octahydro-6-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (XVI), a *cis*-configuration being in line with the observed regeneration of *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-8-methoxy-1 : 4-dioxochrysene (III) in similar circumstances from a solution of *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) in chloroformic hydrogen chloride.[1] It is of interest to note that the same compound, m. p. 171—172°, was the only substance isolable when the *cis*-diketone (VII) was treated in boiling methanol with a trace of hydrogen chloride, no formation of dimethyl ketal being observed (cf. Part I [1] and below).

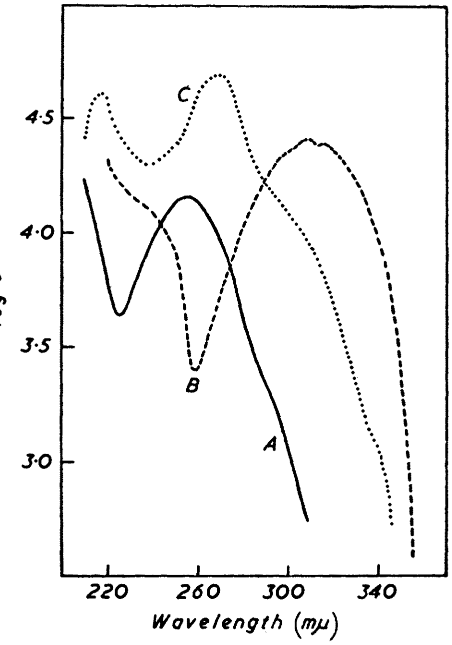


FIG. 1. *Ultraviolet light absorption of* cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (VII) *in alcohol* (*A* ; ——), *of* 7 : 8-*dihydro*-1-*methoxy*-6-p-*methoxyphenylnaphthalene* (XIII) *in hexane* (*B* ; – – – –) *and of* 1-*methoxy*-6-p-*methoxyphenylnaphthalene in hexane* (*C* ; . . . .).

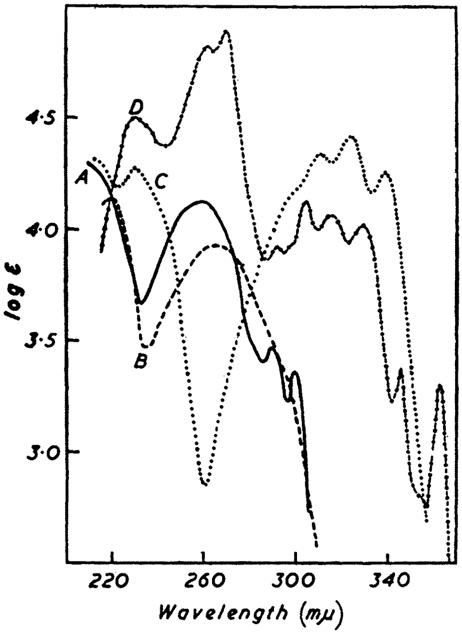
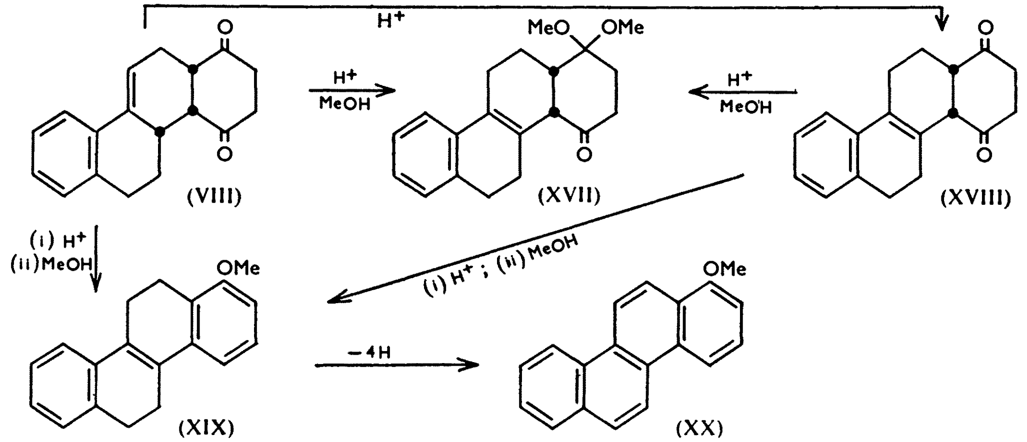


FIG. 2. *Ultraviolet light absorption of* cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*decahydro*-1 : 4-*dioxochrysene* (VIII) *in alcohol* (*A* ; ——), *of* cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*decahydro*-1 : 4-*dioxochrysene* (XVIII) *in alcohol* (*B* ; – – – –), *of* 5 : 6 : 11 : 12-*tetrahydro*-1-*methoxychrysene* (XIX) *in hexane* (*C* ; . . . .), *and of* 1-*methoxychrysene* (XX) *in hexane* (*D* ; — · — · —).

When *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-1 : 4-dioxochrysene (VIII) was heated for a few minutes in methanol containing a trace of hydrogen chloride, the solid product obtained showed by its ultraviolet light absorption spectrum that a shift of the ethylenic double bond from the 11 : 16-position to the 15 : 16-position had occurred. Analysis indicated the presence of two methoxyl groups, and it was evident that ketal formation had taken place very readily, in similar fashion to that previously observed for the 8-methoxy-compound[1] (I), to give, by analogy, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 1-dimethoxy-4-oxochrysene (XVII). Treatment of the diketone (VIII) in cold alcohol-free chloroform with hydrogen chloride, followed by water only, caused a shift in the position of the double bond, as shown by the ultraviolet light absorption spectrum (Fig. 2),[cf. 4b] to give *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dioxochrysene (XVIII), which on treatment in hot methanol with a trace of hydrogen chloride again gave the dimethyl ketal (XVII). Treatment of the diketone (VIII) in alcohol-free chloroform with hydrogen chloride followed by methanol gave in high yield the aromatised product 5 : 6 : 11 : 12-tetrahydro-1-methoxychrysene (XIX), with characteristic *trans*-stilbene-like ultraviolet light absorption properties (Fig. 2) (cf. Part I[1]). The same product (XIX) was also obtained by similar treatment of the *cis*-diketone (XVIII). Dehydrogenation of the product (XIX) with chloranil in boiling anisole gave the known 1-methoxychrysene (XX), identified by its melting point[10] and its ultraviolet light absorption spectrum (Fig. 2).[11]



Similarly, *cis-syn*-1 : 2 : 3 : 10 : 1′ : 2′ : 3′ : 4′-octahydro-1′ : 4′-dioxo-1 : 2-benzofluorene (IX), on brief treatment with boiling methanol containing a trace of hydrogen chloride, afforded a dimethyl ketal, formulated, by analogy,[1] as *cis*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydro-4′ : 4′-dimethoxy-1′-oxo-1 : 2-benzofluorene (XXI). A solution of the diketone (IX) in chloroform developed the characteristic red colour of a halochromic salt on treatment with dry hydrogen chloride, but attempted isolation of the compound analogous to (XVIII), formed by migration of the olefinic double bond, showed the substance to be highly unstable. Addition of methanol, however, to the halochromic salt solution, followed by the usual working-up procedure, gave the product resulting from aromatisation of the dioxo*cyclo*hexane ring, 3 : 4-dihydro-4′-methoxy-1 : 2-benzofluorene (XXII); this was readily dehydrogenated by chloranil in boiling anisole to 4′-methoxy-1 : 2-benzofluorene (XXIII), which has a complex ultraviolet light absorption spectrum (Fig. 3), similar to that of 1 : 2-benzofluorene itself.[12]

Of the eight examples, (I), (III), (VI)—(IX), (X), and (XVIII), that we have now studied, aromatisation of the dioxo*cyclo*hexane ring has been observed to take place readily in every case except those of (VI) and the stereoisomeric (X), and the reason for the poorer conversion in these cases may be primarily lack of mobility of the 6 : 7-double bond reducing the tendency for conversion into the conjugated system necessary for

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[10] Berenblum and Schoental, *Biochem. J.*, 1949, **44**, 604.
[11] Holiday and Jope, *Spectrochim. Acta*, 1950, **4**, 157.
[12] Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634.

halochromic salt formation, since in each case, with the exception of (VI) and (X), a characteristic colour typical of halochromic salt formation was observed on treatment of chloroform solutions of the starting materials with hydrogen chloride. Ketal formation in hot methanol in the presence of a trace of hydrogen chloride, when it took place, took place with great ease, but it has only been observed with the tetracyclic compounds (I),[1] (III),[1] (VIII), (IX), and (XVIII), and may be related to coplanarity of the aromatic nucleus with the rest of the conjugated system in the halochromic salts in these cases caused by the ethylene, or, in the case of (IX), by the methylene, bridge.

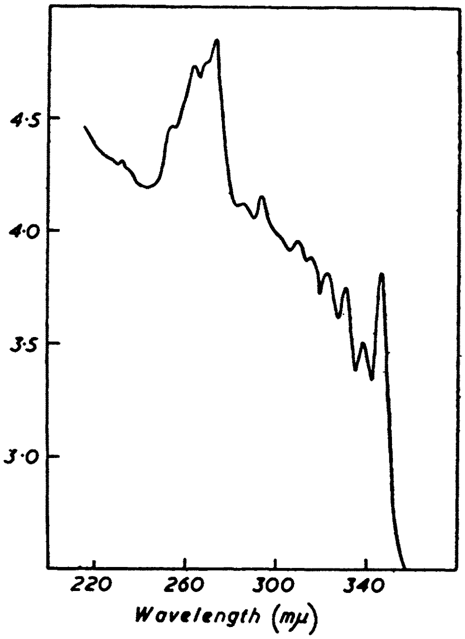
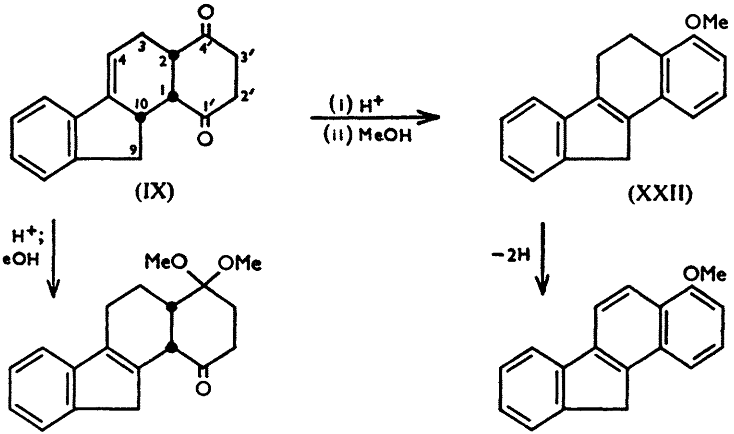


FIG. 3. *Ultraviolet light absorption of 4′-methoxy-1 : 2-benzofluorene* (XXIII) *in hexane.*



(IX)

(XXII)

(XXI)

(XXIII)

EXPERIMENTAL

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

Preparation of Ethynylcarbinols.—General method. The method[4b] used for the reaction between 6-methoxy-1-tetralone and lithium acetylide in liquid ammonia at room temperature in the presence of a large excess of free acetylene was employed with minor modifications which are noted in the following four paragraphs.

(a) 2-*Phenylbut*-3-*yn*-2-*ol*. Acetophenone (60 g., 0·5 mole) in ether (70 c.c.) was added to lithium acetylide (from 1 g.-atom of lithium) in liquid ammonia. Crystallisation of the crude product from pentane afforded 2-phenylbut-3-yn-2-ol as prisms (34·3 g.), m. p. 48—49°. Acetophenone was recovered as the semicarbazone (16·5 g.) from the mother-liquors, and a second crop of the alcohol (9·8 g.) was then isolated (total yield, 44·1 g.; conversion, 60%). Oroshnik and Mebane [5c] record m. p. 48·5—50° and a yield of 82% (conversion, 29%) using lithium acetylide, or 77% (conversion, 47%) using calcium acetylide, while Nazarov and Kotlyarevsky [5d] record a yield of 46% using ethynylmagnesium bromide.

(b) 2-p-*Methoxyphenylbut*-3-*yn*-2-*ol*. *p*-Methoxyacetophenone (75 g., 0·5 mole) in ether (50 c.c.) and lithium acetylide (from 1 g.-atom of lithium) afforded this *alcohol*, which separated from benzene–light petroleum (b. p. 40—60°) in colourless prisms (59·4 + 9·3 g.; conversion, 78%), m. p. 41°, depressed to below room temperature on admixture with *p*-methoxyacetophenone (m. p. 38—39°) (Found: C, 74·6; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). Nazarov and Kotlyarevsky [5d] claim a 30% yield using ethynylmagnesium bromide but no physical properties or analysis of their product is recorded. Hofstetter and Wilder Smith [13] record a yield of 73% of the homologous 3-*p*-methoxyphenylpent-1-yn-3-ol using sodium acetylide in dioxan at room temperature.

(c) 1-*Ethynyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*. The crude product, obtained from 1-tetralone (36·5 g., 0·25 mole) in ether (50 c.c.) and lithium acetylide (from 0·5 g.-atom of lithium), failed to crystallise, and was treated directly with semicarbazide (0·25 mole), affording crude 1-tetralone semicarbazone (23·0 g.). The non-ketonic portion was distilled in a vacuum to give 1-ethynyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol, b. p. 88—93°/0·001 mm., partly solidifying to a low-melting solid (24·2 g.; 57% conversion) (Found: C, 83·5; H, 6·9. Calc. for $C_{12}H_{12}O$: C, 83·7; H, 7·0%). Goldberg and Muller [14] record b. p. 104°/0·2 mm.

(d) 1-*Ethynylindan*-1-*ol*. Unchanged ketone was separated as the semicarbazone (15·1 g.) from the reaction between indan-1-one (26·4 g., 0·2 mole), added in ether (25 c.c.), and lithium acetylide (from 0·25 g.-atom of lithium) in liquid ammonia, and 1-*ethynylindan*-1-*ol*, isolated in the usual way after semicarbazide treatment of the crude product, separated from light petroleum in fine colourless needles (6·4 g.; 20% conversion), m. p. 72—74° (Found: C, 83·3; H, 6·7. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%). This substance readily sublimed at atmospheric pressure, and co-distillation with solvent may have accounted in part for the low recovery.

*Preparation of Diene–*p*-Benzoquinone Addition Products.—General method.* The method outlined [4b] for the preparation of *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1 : 4-dioxochrysene from 1-ethynyl-1 : 2 : 3 : 4-tetrahydro-1-hydroxy-6-methoxynaphthalene by partial hydrogenation of the latter using the Lindlar [7] catalyst to the 1-vinyl compound, followed by dehydration with iodine in boiling benzene [8] to 3 : 4-dihydro-6-methoxy-1-vinylnaphthalene and addition of *p*-benzoquinone to the latter compound without isolation of intermediate products, was applied to the above series of ethynylcarbinols.

(a) cis-1 : 4 : 5 : 8 : 9 : 10-*Hexahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene*. Catalytic hydrogenation of 2-phenylbut-3-yn-2-ol to 2-phenylbut-3-en-2-ol, b. p. 50—51°/0·4 mm., n_D^{21} 1·5378, proceeded normally (Found: C, 81·0; H, 8·2. Calc. for $C_{10}H_{12}O$: C, 81·1; H, 8·1%); Martin [15] records b. p. 95°/13 mm., n_D^{19} 1·5320. The vinylcarbinol could not be dehydrated by the Hibbert method,[8] being recovered unchanged, while other methods tried gave polymeric material and the necessary diene was therefore prepared by the method of Price, Benton, and Schmidle.[3] A solution of 2-phenyl-1 : 3-butadiene (20·34 g.) in methanol (70 c.c.) was treated with *p*-benzoquinone (15·6 g.) added in portions with stirring. The clear solution was set aside overnight and the crystalline adduct was then collected. Crystallisation from benzene–light petroleum afforded cream-coloured needles (25·8 g.) of cis-1 : 4 : 5 : 8 : 9 : 10-*hexahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene*, m. p. 121—122° (Found: C, 80·8; H, 5·7. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

(b) cis-1 : 4 : 5 : 8 : 9 : 10-*Hexahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene*. 2-*p*-Methoxyphenylbut-3-yn-2-ol (8·8 g., 0·05 mole) was hydrogenated in the usual way. Dehydration with iodine in benzene proceeded very slowly and two further additions of a small crystal of

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[13] Hofstetter and Wilder Smith, *Helv. Chim. Acta*, 1953, **36**, 1706.

[14] Goldberg and Muller, *ibid.*, 1940, **23**, 831.

[15] Martin, *Compt. rend.*, 1956, **242**, 1486.

iodine were necessary in the course of 24 hr. (Found : Water, 0·8 c.c. Calc. : 0·9 c.c.). The crude adduct (6·55 g.) contained some insoluble high-melting material, and crystallisation from ethyl acetate afforded cis-1 : 4 : 5 : 8 : 9 : 10-*hexahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene*, pinkish-brown needles (2·65 g.), m. p. 129—131° (decomp.) (Found : C, 76·3; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

(c) cis-syn-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Octahydro*-1 : 4-*dioxochrysene*. Catalytic hydrogenation of the ethynyltetralol (15·33 g.) afforded 1 : 2 : 3 : 4-*tetrahydro*-1-*vinyl*-1-*naphthol*; a purified specimen had b. p. 82·5°/0·4 mm., n_D^{21} 1·5618, and solidified at 0° (Found : C, 82·8; H, 8·1. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%). Dehydration of the vinyltetralol required 7 hr. (Found : Water, 1·25 c.c. Calc. : 1·60 c.c.). After reaction with *p*-benzoquinone (1 equiv.), crystallisation from ethyl acetate–light petroleum afforded *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-1 : 4-dioxochrysene, pale yellow needles (9·85 g.), m. p. 142—144° (Found : C, 81·6; H, 6·4. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%). Dane *et al.*[16] record m. p. 145—146°.

(d) cis-syn-1 : 2 : 3 : 10 : 1′ : 4′-*Hexahydro*-1′ : 4′-*dioxo*-1 : 2-*benzofluorene*. 1-Ethynylindan-1-ol (3·74 g.) was hydrogenated and the product was dehydrated (2·5 hr.) (Found : Water, 0·39 c.c. Calc. : 0·43 c.c.). Reaction with *p*-benzoquinone (1 equiv.) and crystallisation of the product from ethyl acetate–chloroform afforded cis-syn-1 : 2 : 3 : 10 : 1′ : 4′-*hexahydro*-1′ : 4′-*dioxo*-1 : 2-*benzofluorene*, pale-yellow needles (3·7 g.), m. p. 189—195° (decomp. in sealed evacuated capillary) (Found : C, 81·2; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

*Reduction of Diene–*p*-Benzoquinone Addition Products with Zinc and Glacial Acetic Acid.*—(a) cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene* (VI). *cis*-1 : 4 : 5 : 8 : 9 : 10-Hexahydro-1 : 4-dioxo-6-phenylnaphthalene (15 g.) in glacial acetic acid (450 c.c.) was treated with shaking and cooling under running water with zinc powder (15 g.) added in portions during 5 min. A second quantity of zinc powder (15 g.) was then added all at once and shaking was continued for a further 5 min. After removal of unchanged zinc, the filtrate was poured into water (2 l.) and extracted three times with chloroform. The combined extracts were washed with water, with dilute aqueous sodium hydrogen carbonate solution, and finally with water, dried, and evaporated under reduced pressure. Crystallisation of the residue from methanol gave cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene* (VI) in the form of colourless needles (13·2 g.), m. p. 116—117° (Found : C, 80·0; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). Ultraviolet light absorption : $\lambda_{max.}$ 245 mμ; log ε 4·06.

(b) cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (VII). In a similar manner *cis*-1 : 4 : 5 : 8 : 9 : 10-hexahydro-6-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (2·4 g.) was reduced in glacial acetic acid (200 c.c.) with zinc powder (2 × 2·4 g.). Crystallisation of the product from benzene–light petroleum afforded cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (VII) in the form of colourless needles (2·0 g.), m. p. 139—141° (Found : C, 75·6; H, 6·6. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). Ultraviolet light absorption : $\lambda_{max.}$ 255 mμ; log ε 4·16 (Fig. 1).

(c) cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-1 : 4-*dioxochrysene* (VIII). *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-Octahydro-1 : 4-dioxochrysene (12·2 g.) was reduced in acetic acid (300 c.c.) with zinc powder (2 × 12·2 g.). The entire reaction mixture was poured into water and extracted three times with chloroform. The filtered extracts were combined and washed as before. The dried chloroform solution was evaporated to small bulk under reduced pressure and addition of methanol then gave cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*decahydro*-1 : 4-*dioxochrysene* (VIII) in the form of fine needles (11·66 g.), m. p. 156—157° (Found : C, 81·5; H, 6·9. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%). Ultraviolet light absorption : $\lambda_{max.}$ 260, 290, 300 mμ; log ε 4·13, 3·47, and 3·36 respectively (Fig. 2).

(d) cis-syn-1 : 2 : 3 : 10 : 1′ : 2′ : 3′ : 4′-*Octahydro*-1′ : 4′-*dioxo*-1 : 2-*benzofluorene* (IX). *cis-syn*-1 : 2 : 3 : 10 : 1′ : 4′-Hexahydro-1′ : 4′-dioxo-1 : 2-benzofluorene (7·2 g.) was reduced in a mixture of benzene (500 c.c.) and glacial acetic acid (400 c.c.) with zinc powder (2 × 7·2 g.). After removal of the zinc, the filtrate was poured into much water, and the precipitated product was redissolved by addition of chloroform and washed in the usual way. Crystallisation, from chloroform–methanol, of the solid residue left on evaporation afforded cis-syn-1 : 2 : 3 : 10 : 1′ : 2′ : 3′ : 4′-*octahydro*-1′ : 4′-*dioxo*-1 : 2-*benzofluorene* (IX) in the form of needles (6·34 g.), m. p. 218—221° (decomp.) after sintering above 205° (in sealed evacuated capillary) (Found : C, 80·4; H, 6·2. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%). Ultraviolet light absorption : $\lambda_{max.}$ 254, 291, 300 mμ; log ε 4·13, 3·72, and 3·65 respectively.

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[16] Dane, Höss, Bindseil, and Schmitt, *Annalen*, 1937, **532**, 39.

Effect of Hydrogen Chloride and Methanol on cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene* (VI). trans-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene* (X) *and* 7 : 8-*Dihydro*-1-*methoxy*-6-*phenylnaphthalene* (XI).—A solution of *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene (VI) (5·0 g.) in alcohol-free chloroform (25 c.c.) was cooled in ice and saturated with dry hydrogen chloride. The resulting pale yellow solution was treated with methanol (5 c.c.) and kept at room temperature overnight. The chloroform solution, which then showed a pale blue fluorescence in ultraviolet light, was washed with water (twice), with dilute aqueous sodium hydrogen carbonate, and finally with water, dried, and evaporated under reduced pressure with gentle warming only. (This working-up procedure was followed in all hydrogen chloride–chloroform treatments and is subsequently designated " in the usual way "). The resulting residue, on crystallisation from methanol, afforded trans-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene* (X) in the form of colourless leaflets (2·24 g.), m. p. 145—148° (Found : C, 79·9; H, 6·9. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). The same *trans*-isomer (X) was obtained when the *cis*-isomer (VI) in benzene solution was allowed to percolate down a column of alkaline alumina and eluted by the same solvent.

The mother liquors from the *trans*-diketone (X) (above) were taken to dryness and the residue (2·3 g.), an uncrystallisable brown oil, was taken up in benzene–light petroleum (b. p. 40—60°) (1 : 1) and allowed to percolate down a column of activated alumina (20 g.) (Peter Spence and Sons, Ltd., type H). Elution with the same solvent removed a strongly blue-fluorescent band, and evaporation of the eluate gave a colourless fluorescent oil (1·10 g.), which solidified, and crystallisation from benzene–methanol, or from light petroleum (b. p. 40—60°), afforded 7 : 8-*dihydro*-1-*methoxy*-6-*phenylnaphthalene* (XI) in the form of leaflets (0·33 g.), m. p. 80—82°, identical with a synthetic specimen (see below) (Found : C, 86·6; H, 7·1; MeO, 12·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8; MeO, 13·0%). Ultraviolet light absorption in hexane : $\lambda_{max.}$ 238 (infl.), 303 mμ; log ε 4·27, 4·28. The substitution of hydrogen bromide for hydrogen chloride gave a similar result, and the *trans*-diketone (X) (1 g.) could be treated with hydrogen chloride in chloroform, and then with methanol, to give again 7 : 8-dihydro-1-methoxy-6-phenylnaphthalene (XI) (60 mg.).

The dihydronaphthalene (XI) (200 mg.) was dehydrogenated by chloranil (400 mg.; 2 equiv.) in refluxing anisole (25 c.c.) for 16 hr. After cooling and dilution with benzene, the solution was washed with aqueous alkaline sodium dithionite, and then with water, and evaporated under reduced pressure. On crystallisation from benzene–methanol the solid residue afforded 1-*methoxy*-6-*phenylnaphthalene* in the form of plates, m. p. 84—85° (Found : C, 87·1; H, 6·3; MeO, 13·4. $C_{17}H_{14}O$ requires C, 87·1; H, 6·0; MeO, 13·2%). Ultraviolet light absorption in hexane : $\lambda_{max.}$ 257, *ca.* 285 (infl.) mμ; log ε 4·70 and 3·88.

Effect of Hydrogen Chloride and Methanol, and of Hydrogen Chloride followed by Water, on cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (VII). (?)cis-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*Octahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (XVI) *and* 7 : 8-*Dihydro*-1-*methoxy*-6-p-*methoxyphenylnaphthalene* (XIII).—(a) *Methanolic hydrogen chloride.* The compound (VII) (100 mg.) was dissolved in boiling methanol (3 c.c.) with the aid of a few drops of benzene. After the addition of two drops of saturated methanolic hydrogen chloride, the solution was kept at the b. p. for 5 min., during which some concentration took place. On cooling, the yellow solution deposited (?)cis-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydro*-6-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (XVI) in the form of leaflets (80 mg.), m. p. 171—172° (Found : C, 75·4; H, 6·7; MeO, 12·1. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7; MeO, 11·5%). Ultraviolet light absorption : $\lambda_{max.}$ 255 mμ; log ε 4·19.

(b) *Hydrogen chloride in chloroform, followed by water.* A solution of the compound (VII) (0·5 g.) in alcohol-free chloroform (20 c.c.) was saturated with dry hydrogen chloride at 0°, kept at room temperature for 1 hr., and then worked up in the usual way, no methanol being used in this instance. Crystallisation of the solid residue from methanol afforded (?)*cis*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-octahydro-6-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (XVI) (0·29 g.), identical with that prepared as above, and also with a specimen obtained by allowing a solution of the *cis*-isomer (VI) in benzene–light petroleum (b. p. 40—60°) (1 : 1) to percolate down a column of alkaline alumina (20 g.), followed by elution with benzene.

(c) *Hydrogen chloride in chloroform, followed by methanol.* A solution of the compound (VII) (1·58 g.) in alcohol-free chloroform (30 c.c.) was saturated with dry hydrogen chloride at 0°. Methanol (1·5 c.c.) was added to the red solution and the mixture was kept at room temperature overnight. The usual working-up procedure gave a solid residue, and crystallisation from benzene–methanol afforded 7 : 8-*dihydro*-1-*methoxy*-6-p-*methoxyphenylnaphthalene* (XIII) in the form of thin plates (1·0 g.), m. p. 95°, identical with a synthetic specimen (see below) (Found: C, 81·4; H, 6·8; MeO, 22·6. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8; 2MeO, 23·3%). Ultraviolet light absorption in hexane: $\lambda_{max.}$ 238 (infl.), 301 (infl.), 308, 314 mμ; log ε 4·10, 4·36, 4·40, and 3·98 respectively (Fig. 1).

Dehydrogenation of the dihydronaphthalene (XIII) (0·5 g.) in boiling anisole (25 c.c.) with chloranil (0·7 g.; 1·5 equiv.) for 7 hr. yielded a product which crystallised from benzene–methanol to give 1-*methoxy*-6-p-*methoxyphenylnaphthalene* in the form of leaflets (0·36 g.), m. p. 111° (Found: C, 81·7; H, 6·0; MeO, 22·9. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; 2MeO, 23·5%). Ultraviolet light absorption in hexane: $\lambda_{max.}$ 217, 269, 298 (infl.) mμ; log ε 4·60, 4·70, and 4·10 respectively (Fig. 1).

Effect of Hydrogen Chloride and Methanol, and of Hydrogen Chloride followed by Water, on cis-syn-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-*Decahydro*-1 : 4-*dioxochrysene* (VIII). cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*Decahydro*-1 : 1-*dimethoxy*-4-*oxochrysene* (XVII), cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*Decahydro*-1 : 4-*dioxochrysene* (XVIII), *and* 5 : 6 : 11 : 12-*Tetrahydro*-1-*methoxychrysene* (XIX).—(a) *Methanolic hydrogen chloride.* The compound (VIII) (100 mg.) was dissolved in boiling methanol (5 c.c.) by the addition of two drops of saturated methanolic hydrogen chloride (2—3 min.). On cooling, the yellow solution deposited cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*decahydro*-1 : 1-*dimethoxy*-4-*oxochrysene* (XVII) in the form of needles (40 mg.), m. p. 136—138° (Found: C, 77·1; H, 7·8; MeO, 20·6. $C_{20}H_{24}O_3$ requires C, 76·9; H, 7·7; 2MeO, 19·8%). Ultraviolet light absorption: $\lambda_{max.}$ 220, 224 (infl.), 263 mμ; log ε 4·26, 4·16, and 4·04 respectively.

(b) *Hydrogen chloride in chloroform, followed by water.* A solution of the compound (VIII) (1·0 g.) in alcohol-free chloroform (40 c.c.) was saturated with dry hydrogen chloride at 0°. After 2 hr. at room temperature the red solution was worked up in the usual way. The solid residue, crystallised from benzene–light petroleum, afforded cis-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-*decahydro*-1 : 4-*dioxochrysene* (XVIII) in the form of colourless prisms (0·48 g.), m. p. 164—165° (Found: C, 81·0; H, 6·7. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%). Ultraviolet light absorption: $\lambda_{max.}$ 220, 265 mμ; log ε 4·14, 3·92 (Fig. 2). The diketone (VIII), when pure, could be crystallised unchanged from methanol–chloroform but on the addition of a drop of saturated methanolic hydrogen chloride to the hot solution the solution became yellow and, on cooling, deposited the 1 : 1-dimethyl ketal (XVII), m. p. 135—137°, described in (a) (above).

(c) *Hydrogen chloride in chloroform, followed by methanol.* A solution of the diketone (VIII) (3·0 g.) in alcohol-free chloroform (120 c.c.) was saturated at 0° with dry hydrogen chloride. Addition of methanol (3 c.c.) to the yellow solution caused a colour change to orange, which darkened to brown at room temperature overnight, and a clear oil with a greenish fluorescence separated on the surface of the chloroform. After the usual working up, the tarry residue was extracted several times with boiling light petroleum (b. p. 40—60°), and the combined extracts, on concentration, afforded 5 : 6 : 11 : 12-*tetrahydro*-1-*methoxychrysene* (XIX) in the form of leaflets (1·50 g.), m. p. 84—85° (Found: C, 87·0; H, 6·8; MeO, 11·9. $C_{19}H_{18}O$ requires C, 87·0; H, 6·9; MeO, 11·8%). Ultraviolet light absorption in hexane: $\lambda_{max.}$ 231, 299 (infl.), 311, 324, 340 mμ; log ε 4·28, 4·16, 4·34, 4·42, and 4·25 respectively (Fig. 2). On similar treatment, *cis*-1 : 2 : 3 : 4 : 5 : 6 : 11 : 12 : 13 : 14-decahydro-1 : 4-dioxochrysene (XVIII) afforded the same 5 : 6 : 11 : 12-tetrahydro-1-methoxychrysene (XIX).

Dehydrogenation of the tetrahydro-1-methoxychrysene (XIX) (0·5 g.) in boiling anisole (25 c.c.) with chloranil (1·4 g.; 3 equiv.) for 16 hr. gave, after dilution with benzene, washing with aqueous alkaline sodium dithionite, and evaporation of the solvent, a solid residue. Crystallisation from benzene–light petroleum afforded 1-methoxychrysene (XX) in the form of plates (400 mg.), m. p. 182—183° (Found: C, 88·7; H, 5·7; MeO, 12·6. Calc. for $C_{19}H_{14}O$: C, 88·4; H, 5·6; MeO, 12·0%). Berenblum and Schoental[10] record m. p. 185—186°. (4-Methoxychrysene[17] has m. p. 102—103°.) The complex ultraviolet light absorption in hexane agreed closely with that recorded by Holiday and Jope:[11] $\lambda_{max.}$ 230, 262, 270, 292, 305, 316, 329, 346, and 363 mμ; log ε 4·50, 4·82, 4·96, 3·92, 4·13, 4·08, 4·01, 3·34, and 3·31 respectively (Fig. 2).

Effect of Hydrogen Chloride and Methanol, and of Hydrogen Chloride followed by Water, on cis-syn-1 : 2 : 3 : 10 : 1′ : 2′ : 3′ : 4′-*Octahydro*-1′ : 4′-*dioxo*-1 : 2-*benzofluorene* (IX),

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[17] Cook and Schoental, *J.*, 1945, 288.

cis-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : *4′-Octahydro-4′* : *4′-dimethoxy-*1′*-oxo-*1 : *2-benzofluorene* (XXI) *and* 3 : *4-Dihydro-4′-methoxy-*1 : *2-benzofluorene* (XXII).—(a) *Methanolic hydrogen chloride.* A suspension of the diketone (IX) (100 mg.) in methanol (3 c.c.) was heated to boiling and treated with two drops of saturated methanolic hydrogen chloride. After 2—3 min. at the b. p. the solid dissolved completely to give a yellow solution. On cooling, needles (70 mg.; m. p. 168—170°) separated. Recrystallisation from methanol–chloroform afforded the *dimethoxy-compound* (XXI), m. p. 172—174° (Found: C, 76·3; H, 7·4; MeO, 19·8. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·4; 2MeO, 20·8%). Ultraviolet light absorption: $\lambda_{\max.}$ 258 mμ; log ε 4·14.

(b) *Hydrogen chloride in chloroform, followed by water.* By following the method used for the chrysene homologue (above), a yellow gum was obtained which failed to crystallise and which rapidly darkened in air.

(c) *Hydrogen chloride in chloroform, followed by methanol.* A solution of the diketone (IX) (1·0 g.) in alcohol-free chloroform (50 c.c.) was saturated at 0° with dry hydrogen chloride. The resulting red solution was treated at room temperature with methanol (1 c.c.) and kept at room temperature overnight. Working-up in the usual way gave a solid which did not crystallise readily; it was taken up in benzene–light petroleum (b. p. 40—60°) (1 : 2) and allowed to percolate down a column of activated alumina (25 g.). Elution with the same solvent and evaporation of the eluate gave a solid residue (0·67 g.), and crystallisation from light petroleum afforded 3 : *4-dihydro-4′-methoxy-*1 : *2-benzofluorene* (XXII) in the form of needles (0·60 g.), m. p. 108—108·5°, resolidifying on cooling and remelting at 120—121° (Found: C, 87·4; H, 6·4; MeO, 11·9. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5; MeO, 12·5%). Ultraviolet light absorption: $\lambda_{\max.}$ 233, *ca.* 300 (infl.), 309, 323, 339 mμ; log ε 4·34, 4·24, 4·40, 4·48, and 4·29 respectively.

Dehydrogenation of the compound (XXII) (400 mg.) in boiling anisole (20 c.c.) with chloranil (440 mg., 1·1 equiv.) for 7 hr., and isolation of the product by using alkaline sodium dithionite as described above, gave a dark solid which did not crystallise well. Percolation of a solution in benzene down a column of activated alumina (10 g.) and elution with the same solvent gave a colourless solid. Crystallisation from benzene–light petroleum then afforded *4′-methoxy-*1 : *2-benzofluorene* (XXIII) in the form of plates (130 mg.), m. p. 151—152° (Found: C, 87·8; H, 5·7; MeO, 12·9. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7; MeO, 12·6%). Ultraviolet light absorption in hexane: $\lambda_{\max.}$ 231, 254, 263, 269 (infl.), 273, 286, 293, 309, 315, 323, 330, 338, 346 mμ; log ε 4·31, 4·47, 4·73, 4·74, 4·85, 4·12, 4·16, 3·96, 3·88, 3·82, 3·74, 3·51, and 3·82 respectively (Fig. 3).

Synthesis of 7 : *8-Dihydro-*1*-methoxy-*6*-phenylnaphthalene* (XI).—A solution of 5-methoxy-2-tetralone[18] (3·0 g.) in dry ether (30 c.c.) was added dropwise to a boiling solution of phenylmagnesium bromide [from bromobenzene (5·36 g.) and magnesium (0·83 g.)] in ether (50 c.c.), and the mixture was heated under reflux for a further ½ hr., cooled, and decomposed with ice and dilute sulphuric acid. The ether layer was washed, dried, and evaporated to give a pale yellow oil (5·0 g.), which still contained some ketonic material. In one experiment the oil partly crystallised on treatment with methanol, affording 5 : 6 : 7 : *8-tetrahydro-*6*-hydroxy-*1*-methoxy-*6*-phenylnaphthalene* in the form of colourless prisms, m. p. 130—131° (Found: C, 80·3; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). The yellow oil was heated under reflux with anhydrous formic acid (25 c.c.) for ½ hr., the mixture was cooled and poured into water, and the product was recovered in ether. Evaporation of the ether and crystallisation of the solid residue (3·76 g.) from methanol afforded 7 : 8-dihydro-1-methoxy-6-phenylnaphthalene (XI), m. p. 81—82°, identical with that previously described; identity was confirmed by comparison of the infrared absorption spectra of the two specimens.

Synthesis of 7 : *8-Dihydro-*1*-methoxy-*6-p-*methoxyphenylnaphthalene* (XIII).—In a similar manner, 5-methoxy-2-tetralone (3·0 g.) was allowed to react with *p*-methoxyphenylmagnesium bromide [from *p*-bromoanisole (6·4 g.) and magnesium (0·83 g.)] to give 7 : 8-dihydro-1-methoxy-6-*p*-methoxyphenylnaphthalene (XIII), which crystallised from benzene–methanol in plates (1·37 g.), m. p. 94—95°, identical with that described above; identity was confirmed by comparison of the infrared absorption spectra of the two specimens.

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[18] Cornforth, Cornforth, and Robinson, *J.*, 1942, 689.