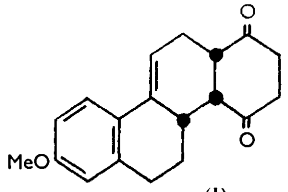
74. *A New and Specific Aromatisation Reaction. Part III.* Aromatisation of Isolated* 1 : 4-*Dioxo*cyclo*hexane Rings.*

By P. A. Robins and James Walker.

The aromatisation of a 1 : 4-dioxo*cyclo*hexane ring to give an alkyl aryl ether in presence of chloroformic hydrogen chloride and an alcohol (Parts I and II) is now shown to occur, though only to a limited extent, in compounds in which this ring remains isolated from a centre of unsaturation. The olefinic double bond in the examples now described does not migrate into conjugation with the newly created aromatic ring. These observations are taken to illustrate the separate occurrence of the later phases of the mechanism already proposed (Part I).

In Part I * we described the ready and extensive conversion of *cis-syn*-1 : 2 : 3 : 4 : 5 : 6 : 12 : 13 : 14 : 15-decahydro-8-methoxy-1 : 4-dioxochrysene (I) into 1-alkoxy-5 : 6 : 11 : 12-tetrahydro-8-methoxychrysenes (II) by the action of chloroformic hydrogen chloride and an alcohol, and a mechanism was proposed in which the halochromic salt (III), containing an extended conjugated system, was postulated as a precursor of the dialkoxytetrahydrochrysene (II). The latter (II; R = Et) was first obtained [1] as a by-product in the conversion of the diketone (I) into the isomeric $\Delta^{15:16}$-unsaturated ketone (IV) with hydrochloric acid in ethanol–chloroform, and this conversion was considered (Part I) to be the first stage in the conversion of the diketone (I) into the halochromic salt (III) and thence into the dialkoxytetrahydrochrysene (II). Similar aromatisations of the 1 : 4-dioxo*cyclo*hexane ring were demonstrated (Part II) in the



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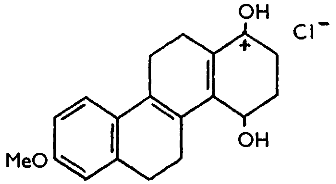

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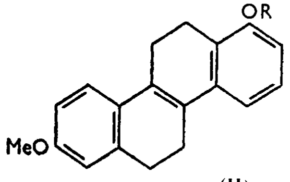

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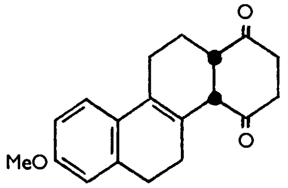

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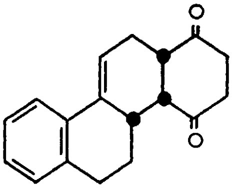

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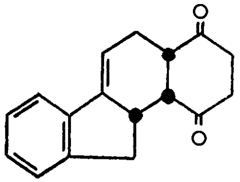

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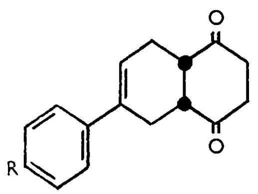

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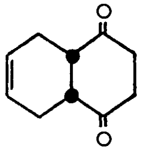
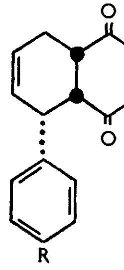


(VIII)



(IX)

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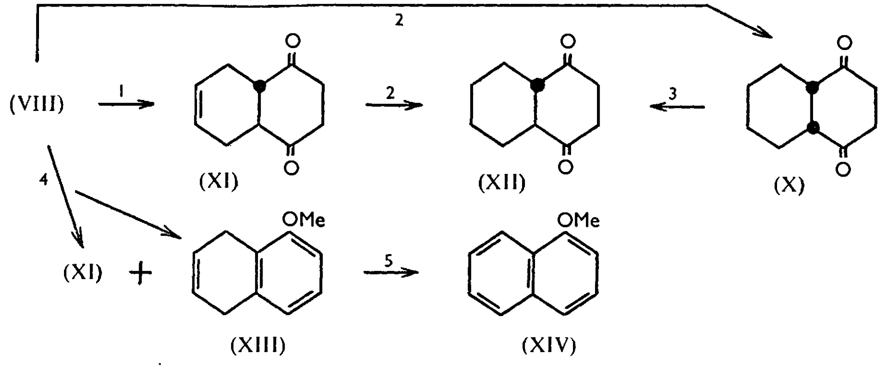
* Part I, *J.*, 1956, 3260; Part II, *J.*, 1957, 177.

[1] Robins and Walker, *J.*, 1956, 3249.

compounds (V), (VI), and (VII; R = H or MeO); each conversion took place in high yield, except that of the substance (VII; R = H), with which concomitant formation of a stereoisomeric diketone was observed. The low conversion in this one case was tentatively ascribed to inherent lack of mobility of the 6 : 7-double bond, rendering difficult the creation of the conjugated system necessary for halochromic salt formation. That the 6 : 7-double bond in the compound (VII; R = H) should be less labile than the corresponding double bond in the compound (VII; R = MeO) is in keeping with the lower mobility observed[2] for the 11 : 16-double bond in the dioxohydrochrysene (V) as compared with that in its methoxy-derivative (I). The present communication describes a further study of the exceptional compound (VII; R = H), together with a study of three new examples, *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxonaphthalene (VIII), *cis-syn*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-5-phenylnaphthalene (IX; R = H), and *cis-syn*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-5-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (IX; R = MeO), in which formation of extended conjugated systems and of halochromic salts of the type (III) are structurally impossible. Notwithstanding these structural limitations in the compounds (VIII) and (IX; R = H or MeO) aromatisation of the 1 : 4-dioxo*cyclo*hexane ring occurred in each case, but to a limited extent only, in presence of chloroformic hydrogen chloride and methanol, and the original olefinic double bond remained isolated from the participating centres of reaction.

cis-1 : 4 : 5 : 8 : 9 : 10-Hexahydro-1 : 4-dioxonaphthalene[3,4] was reduced with zinc powder to *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxonaphthalene (VIII), which was described by Alder and Stein[4] and characterised by catalytic hydrogenation to *cis*-perhydro-1 : 4-dioxonaphthalene[4] (X). Treatment of the *cis*-octahydro-diketone (VIII) with chloroformic hydrogen chloride, or, alternatively, passage in solution in light petroleum–benzene down a column of alkaline activated alumina, effected stereochemical equilibration, to give a difficultly separable mixture of the starting material (VIII) and the stereoisomeric *trans*-diketone (XI), affording on catalytic hydrogenation *trans*-perhydro-1 : 4-dioxonaphthalene (XII), identical with a specimen obtained by stereochemical equilibration of the *cis*-perhydro-diketone (X). When, however, methanol was added to the reaction mixture a third product was isolated in about 17% yield. This substance, an oil, had an ultraviolet light absorption spectrum of typical anisole type and gave, after purification through the picrate, analytical figures indicating the formula $C_{11}H_{12}O$. It was therefore 1 : 4-dihydro-5-methoxynaphthalene (XIII), in which the olefinic double bond has remained isolated from the aromatised ring, and dehydrogenation with chloranil afforded methyl α-naphthyl ether (XIV).



Reagents: 1, Al_2O_3 or $HCl–CHCl_3$; 2, $H_2–Pd$; 3, Ac_2O; 4, $HCl–CHCl_3–MeOH$; 5, $-2H$.

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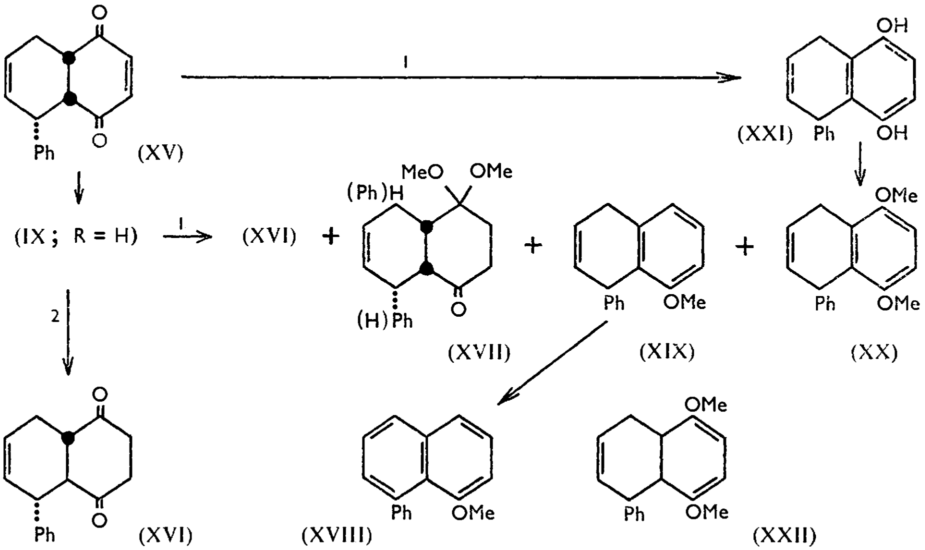
[2] Unpublished observation.
[3] Fieser, *J. Amer. Chem. Soc.*, 1948, **70**, 3165.
[4] Alder and Stein, *Annalen*, 1933, **501**, 247.

cis-syn-1 : 4 : 5 : 8 : 9 : 10-Hexahydro-1 : 4-dioxo-5-phenylnaphthalene [5] (XV) was reduced with zinc to give *cis-syn*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-5-phenylnaphthalene (IX; R = H), whose ultraviolet light absorption spectrum indicated that the 6 : 7-double bond had not migrated into conjugation with the phenyl group; the stereochemical configuration is based on analogy.[6]

Stereochemical equilibration of the diketone (IX; R = H) by passage in solution through alkaline activated alumina gave initially a solid, m. p. 107—110°, which could be recrystallised without change in melting point from relatively concentrated solution and was at first considered to be a stereoisomeride of the diketone (IX; R = H). It was, however, subsequently found to be a mixture from which a pure stereoisomeric (?)*trans-anti*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-5-phenylnaphthalene (XVI), m. p. 124—126°, could be obtained by seeding a dilute solution. The other component of the mixture could not be obtained pure. A similar mixture was obtained when the diketone (IX; R = H) was treated with hydrogen chloride in chloroform and then briefly with methanol. Treatment of the diketone (IX; R = H) with hydrogen chloride in chloroform and then with methanol at room temperature for 3 days gave a complex mixture. The crude product was roughly separated in the first instance into a solid (A) and an oil (B). Recrystallisation and hand-sorting resolved the solid (A) into the stereoisomeric diketone (XVI) already isolated from the stereochemical equilibration of the diketone (IX; R = H), and a substance $C_{16}H_{16}O(OMe)_2$, m. p. 123—124°, which was obviously a ketal (XVII) of the type previously encountered (Parts I and II). An attempt to determine its orientation was, however, unsuccessful. Chromatography of the oil (B) on alumina afforded four main fractions: (i) a substance $C_{17}H_{16}O$, m. p. 104—106°, containing one methoxyl group and having an ultraviolet light absorption spectrum indicative of an unconjugated anisole ring; (ii) a crystalline solid $C_{18}H_{18}O_2$, m. p. 108—110°, containing two methoxyl groups and having an ultraviolet light absorption spectrum indicative of a 1 : 4-dimethoxybenzene ring; (iii) the dimethyl ketal (XVII); and (iv) the *trans*-diketone (XVI).



Reagents: 1, HCl-$CHCl_3$-MeOH; 2, Al_2O_3 or HCl-$CHCl_3$.

The substance $C_{17}H_{16}O$, m. p. 104—106°, was dehydrogenated with chloranil to a compound $C_{17}H_{14}O$, m. p. 55—56°, which could have been either 1-methoxy-5- or -8-phenylnaphthalene (XVIII). An authentic specimen of 1-methoxy-5-phenylnaphthalene,

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[5] Braude, Jones, and Stern, *J.*, 1947, 1087.

[6] Alder, Vagt, and Vogt, *Annalen*, 1949, **565**, 135.

prepared from 5-methoxy-1-tetralone and phenylmagnesium bromide, had m. p. 81—82°, and the difference between this compound and the substance $C_{17}H_{14}O$, m. p. 55—56°, was further demonstrated by differences in the fine structure bands observable in the ultraviolet light absorption spectra of the two substances, which, nevertheless, showed a gross overall similarity (Fig. 1) and were substantially different from the spectra of 1-methoxy-6- (Part II) and 1-methoxy-7-phenylnaphthalene (below). The substance $C_{17}H_{14}O$, m. p. 55—56°, must therefore have been 1-methoxy-8-phenylnaphthalene (XVIII), and its precursor $C_{17}H_{16}O$, m. p. 104—106°, must have been the dihydro-methoxy-phenylnaphthalene (XIX); unfortunately, attempts to synthesise 1-methoxy-8-phenylnaphthalene (XVIII) by a Gomberg or Bamberger free-radical coupling reaction, employing derivatives of 1-amino-8-methoxynaphthalene, gave only intractable tars. The free phenol, obtained on demethylation of the ether (XVIII) with hydrogen iodide in acetic anhydride, could not be obtained crystalline; it gave a strong blue colour with Gibbs's reagent [7] and was cryptophenolic.

FIG. 1. FIG. 2.

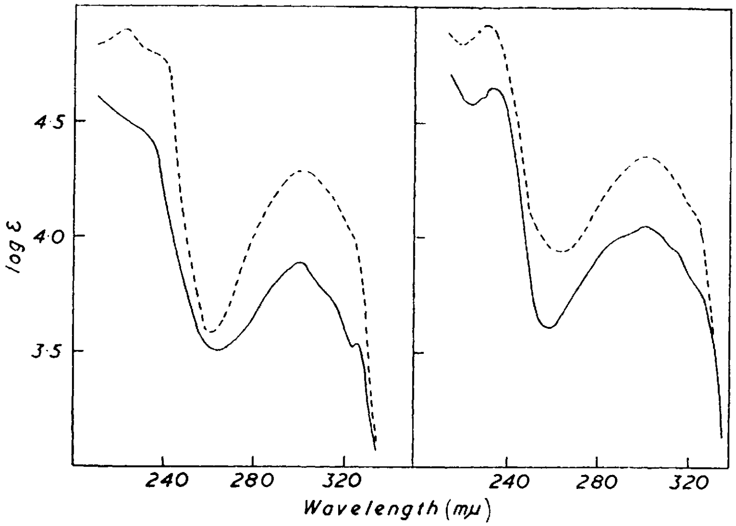

FIG. 1. *Ultraviolet light absorption of 1-methoxy-8-phenylnaphthalene* (XVIII) (——) *and 1-methoxy-5-phenylnaphthalene* (– – – –) *in hexane.*

FIG. 2. *Ultraviolet light absorption of 1-methoxy-8-*p*-methoxyphenylnaphthalene* (XXV) (——) *and 1-methoxy-5-*p*-methoxyphenylnaphthalene* (XXVI) (– – – –) *in hexane.*

For clarity the curves for the 1 : 5-*derivatives are displaced by* + 0·3 in log ε.

The substance $C_{18}H_{18}O_2$, m. p. 108—110°, was shown to be 1 : 4-dihydro-5 : 8-dimethoxy-1-phenylnaphthalene (XX) by comparison with an authentic specimen obtained by methylation of the dihydric phenol (XXI); the mode of formation of the dimethyl ether (XX) from the octahydro-diketone (IX; R = H) in the aromatisation is not clear, but it may have resulted from aerial dehydrogenation of a dihydro-intermediate such as (XXII), which could arise from two metathetic replacements of hydroxyl by alkoxyl of the type indicated in the mechanism already proposed (Part I). The possibility that the dimethyl ether (XX) had arisen from traces of unchanged hexahydro-diketone (XV) in the starting material (IX; R = H) was discounted by the fact that under the conditions of the aromatisation, allowing nearly six days for interaction, only a trace of non-phenolic material was formed from the compound (XV), and that gave no readily eluted fluorescent material on chromatography. It is also of interest that the substance, m. p. 170°, described

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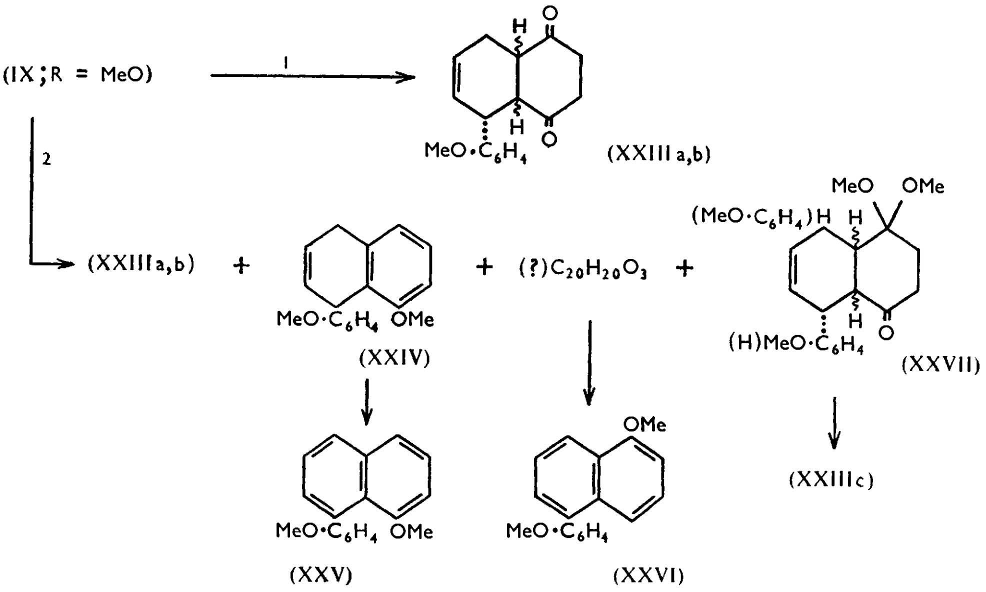
[7] Gibbs, *J. Biol. Chem.*, 1927, **72**, 649.

by Weizmann, Bergmann, and Haskelberg [8] as the hexahydro-diketone (XV) was, in all probability, the dihydric phenol (XXI), m. p. 168—169°, resulting from the vigorous conditions used by these authors for isolation (distillation at 240°/0·2 mm.), and that Braude, Jones, and Stern [5] have reported that this change can take place on storage and is facilitated by exposure to light.

cis-syn-1 : 4 : 5 : 8 : 9 : 10-Hexahydro-5-*p*-methoxyphenyl-1 : 4-dioxonaphthalene [5] was reduced in the usual way to give *cis-syn*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-5-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (IX; R = MeO), and stereochemical equilibration gave a mixture of two new stereoisomeric diketones (XXIIIa), m. p. 164°, and (XXIIIb), m. p. 135—136°. Treatment of the diketone (IX; R = MeO) in chloroform with hydrogen chloride followed by methanol for 24 hr. at room temperature gave the stereoisomeric diketone (XXIIIb) on crystallisation of the crude product. Chromatography of the material recovered from the mother-liquors on alumina gave a readily eluted compound, m. p. 123—124°, which from its analysis and ultraviolet light absorption spectrum appeared to be the expected 1 : 4-dihydro-8-methoxy-1-*p*-methoxyphenylnaphthalene (XXIV); dehydrogenation with chloranil gave 1-methoxy-8-*p*-methoxyphenylnaphthalene (XXV), whose structure followed from similar considerations to those applicable in the case of the corresponding phenyl derivative (XVIII) (above). The dehydrogenation product (XXV) differed from an authentic synthetic specimen of 1-methoxy-5-*p*-methoxyphenylnaphthalene (XXVI) in melting point and in the fine structure bands of its ultraviolet light absorption spectrum, although a gross overall similarity between the two spectra was again apparent (Fig. 2). When the treatment of the diketone (IX; R = MeO) with chloroformic hydrogen chloride and methanol was extended to 3 days a somewhat different result was obtained. Direct crystallisation of the product gave the stereoisomeric diketone (XXIIIa), m. p. 164°, in place of that (XXIIIb) of m. p. 135—136°, together with some of the aromatisation product, 1 : 4-dihydro-8-methoxy-1-*p*-methoxyphenylnaphthalene (XXIV). Chromatography on alumina of the material recovered from the mother-liquors gave (i) a further quantity of the aromatisation product (XXIV), (ii) a small quantity of a substance, m. p. 76—76·5°, apparently $C_{20}H_{20}O_3$, (iii) a trace of the stereoisomeric diketone



Reagents: 1, Al_2O_3 or $HCl–CHCl_3$; 2, $HCl–CHCl_3–MeOH$.

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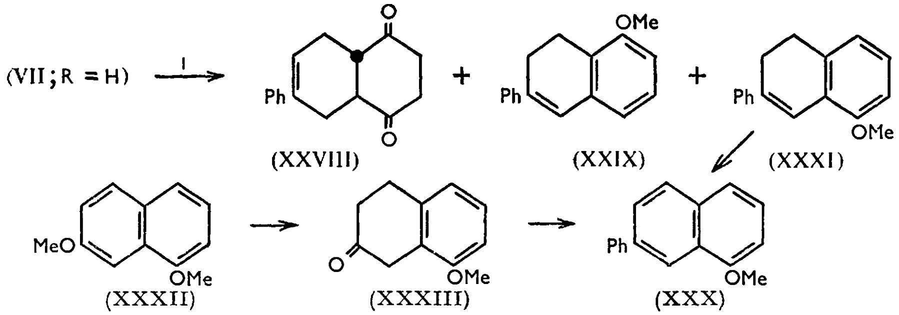
[8] Weizmann, Bergmann, and Haskelberg, *J.*, 1939, 391.

(XXIIIa), m. p. 164°, and (iv) a substance, m. p. 132—133°, which from its analysis and ultraviolet light absorption appeared to be a dimethyl ketal (XXVII) of the type previously encountered. Although the small amount of material available precluded an extensive study, the substance of m. p. 76—76·5° appeared to contain two methoxyl groups; its ultraviolet light absorption spectrum was very similar to that of the aromatisation product (XXIV) but dehydrogenation in the usual way with chloranil afforded 1-methoxy-5-*p*-methoxyphenylnaphthalene (XXVI). The ketal (XXVII), m. p. 132—133°, on hydrolysis with aqueous acetic acid, afforded a fourth stereoisomeric diketone (XXIIIc) of m. p. 155—156°. Apart from the starting material (IX; R = MeO) we are not in a position to assign configurations to these four stereoisomerides (IX; R = MeO) and (XXIII*a*, *b*, *c*).

The formation of an aromatised product in relatively low yield together with stereoisomeric diketone(s) in each of the three examples described above recalled the apparently anomalous behaviour of *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxo-6-phenylnaphthalene(VII; R = H) described in Part II, and this was therefore re-investigated.

It had been found previously in the treatment of the diketone (VII; R = H) overnight with chloroformic hydrogen chloride and then methanol that approximately 20% of crude aromatised product was obtained on chromatography of the material left after separation of the stereoisomeric *trans*-diketone (XXVIII), and on crystallisation of the crude aromatisation product to give 1 : 2-dihydro-8-methoxy-3-phenylnaphthalene (XXIX) a non-crystalline fluorescent oil remained in the mother-liquors. In order to obtain a further quantity of this oil the experiment was repeated on a larger scale and the reaction was allowed to proceed for nearly three days. Crystallisation of the crude product then afforded the aromatised product (XXIX) (*ca.* 16%). The non-crystalline material recovered from the mother-liquors was chromatographed on alumina, affording a readily eluted colourless fluorescent oil (28%), together with other more strongly adsorbed products. Repeated crystallisation of this oily material gave a further quantity of the aromatisation product (XXIX) (5%) and an isomeric compound, m. p. 59—60° (6%), affording on dehydrogenation 1-methoxy-7-phenylnaphthalene (XXX), identical with a synthetic specimen. The compound, m. p. 59—60°, had an ultraviolet light absorption spectrum and gave an analysis consistent with its formulation as 1 : 2-dihydro-5-methoxy-3-phenylnaphthalene (XXXI), but showed slight differences in melting point and infrared absorption spectrum from those of a synthetic specimen, possibly due to the presence of a small proportion of the 1 : 4-dihydro-isomeride. Synthesis of 1-methoxy-7-phenylnaphthalene (XXX) was accomplished in a similar manner to that employed for the 6-phenyl isomer (Part II). Reduction of 1 : 7-dimethoxynaphthalene (XXXII) with sodium and alcohol, followed by acid hydrolysis, gave the previously unknown 8-methoxy-2-tetralone (XXXIII). Reaction with phenylmagnesium bromide and dehydration with formic acid then afforded 1 : 2-dihydro-5-methoxy-3-phenylnaphthalene (XXXI), which, as indicated above, showed



Reagent: I, HCl-CHCl$_3$-MeOH.

slight differences in properties from the product of the aromatisation reaction. Dehydrogenation of the dihydro-compound (XXXI) with chloranil in the usual way gave 1-methoxy-7-phenylnaphthalene (XXX).

The four examples (VIII), (IX; R = H or MeO), and (VII; R = H), in which aromatisation of the 1 : 4-dioxo*cyclo*hexane ring has occurred to a relatively minor extent only under the influence of chloroformic hydrogen chloride and methanol, stand in marked contrast with the examples (I), (IV), (V), (VI), and (VII; R = MeO) described in Parts I and II, in which aromatisation of the 1 : 4-dioxo*cyclo*hexane ring took place rapidly and in high yield. In the latter cases also the olefinic double bond migrated into conjugation with respect to both the pre-existent aryl group and the aromatic ring created in the reaction, in other words the products of the aromatisations described in Parts I and II were of substituted *trans*-stilbene type. The examples (VIII) and (IX) described in the present paper were chosen so as to obviate the fulfilment of similar structural conditions, and aromatisation of the 1 : 4-dioxo*cyclo*hexane ring has been shown to take place in these cases, although only in low yield, without concomitant migration of the olefinic double bond into a position in which it would ultimately be conjugated with the aromatic ring newly created. Furthermore, in the examples discussed in Parts I and II the aromatisation of the 1 : 4-dioxo*cyclo*hexane ring took place to give in high yield exclusively the product predicted by the mechanism outlined in Part I, whereas with at least two [(IX; R = MeO) and (VII; R = H)] of the examples described in the present paper the formation of alternative aromatisation products [(XXIV), (?)$C_{20}H_{20}O_3$, (XXIX), and (XXXI)] from the 1 : 4-dioxo*cyclo*hexane ring was observed; in one case (IX; R = H), the formation of the 1 : 4-dimethoxy-derivative (XX) was also noted.

These observations are taken to indicate that the ability to undergo the present aromatisation reaction is an inherent property of the 1 : 4-dioxo*cyclo*hexane ring, but the occurrence of aromatisation to the much greater extent observed in Parts I and II is attributable to the existence in the examples there discussed of halochromic salts of the type (III) as relatively more stable reaction intermediates than those concerned in aromatisations involving isolated 1 : 4-dioxo*cyclo*hexane rings.

EXPERIMENTAL

Routine ultraviolet light absorption measurements were made in 96% ethanol, unless otherwise stated, on a Unicam S.P. 500 Spectrophotometer. The existence and location of fine-structure features were kindly confirmed by Dr. G. H. Beaven using the photographic logarithmic cam method.[9] Light petroleum refers to the fraction of boiling range 60—80°, unless otherwise stated.

cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxonaphthalene* (VIII).—*p*-Benzoquinone (65 g.) and freshly distilled butadiene (40 g.) were allowed to react in glacial acetic acid (300 c.c.) in the manner described by Fieser.[3] The product, without isolation, was reduced by the addition of zinc powder (100 g.) in eight portions at intervals of several minutes with shaking and water-cooling as necessary. At the end of the reaction unused zinc and zinc acetate were removed by filtration and washed with a little benzene. The filtrate was poured into much water, and the product was recovered, washed with aqueous sodium hydrogen carbonate, and dried in benzene. The benzene solution was concentrated to small bulk and treated with an equal volume of light petroleum; *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydro-1 : 4-dioxonaphthalene (VIII) separated in needles (44 g.), m. p. 98—99°, raised to 103—105° by several recrystallisations. Alder and Stein[4] record m. p. 108°.

Stereochemical Equilibration of cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxonaphthalene* (VIII). trans-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxonaphthalene* (XI).—A solution of the *cis*-compound (VIII) (2·0 g.) in alcohol-free chloroform (20 c.c.) was saturated with dry hydrogen chloride at 0° and kept at room temperature overnight. The clear, pale yellow solution was washed successively with water (twice), with aqueous sodium hydrogen carbonate,

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[9] Holiday, *J. Sci. Instr.*, 1937, **14**, 166.

and finally with water, then filtered and evaporated under reduced pressure with gentle warming. (This working-up procedure was followed in all hydrogen chloride–chloroform treatments and is subsequently designated " in the usual way.") The pasty residue was extracted several times with boiling light petroleum, and the extracts were filtered from a small insoluble residue, clarified by the addition of a few drops of ethanol, and set aside. The fine needles that separated afforded, after several crystallisations from light petroleum, trans-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-1 : 4-*dioxonaphthalene* (XI) as colourless plates (0·80 g.), m. p. 96—97° (Found: C, 73·2; H, 7·6. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·4%). The mother-liquors on concentration gave a small quantity of unchanged *cis*-stereoisomer (VIII), m. p. 102—103°.

Catalytic hydrogenation of the *trans*-octahydro-diketone (XI) (0·40 g.) in methanol (20 c.c.) in the presence of 2% palladised strontium carbonate (100 mg.) gave *trans*-perhydro-1 : 4-dioxonaphthalene (XII) (0·32 g.), which separated from light petroleum in leaflets, m. p. 119°. Alder and Stein [4] record m. p. 122° for the saturated *trans*-diketone (XII), prepared by the action of hot acetic anhydride on the saturated *cis*-diketone (X); repetition of this experiment gave a product identical in m. p. and mixed m. p. with our sample described above.

Action of Hydrogen Chloride and Methanol in Chloroform on cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxonaphthalene* (VIII). 1 : 4-*Dihydro*-5-*methoxynaphthalene* (XIII).—A solution of the *cis*-diketone (VIII) (10 g.) in alcohol-free chloroform (200 c.c.) was cooled in ice and saturated with dry hydrogen chloride. The initially non-fluorescent solution then showed a milky-white fluorescence in ultraviolet light. Methanol (10 c.c.) was added and the solution was kept at room temperature for 60 hr. before being worked up in the usual way. The resulting dark brown oil was extracted repeatedly with boiling light petroleum (b. p. 40—60°) until only a small tarry residue remained. The combined extracts on cooling deposited crystals together with a little brown gum. The crystals were of two forms which could be roughly separated by flotation. Repeated recrystallisation from light petroleum gave small quantities of the starting material (VIII) and its *trans*-stereoisomer (XI). The original light petroleum extracts, after separation of the crystalline material, showed a pale blue fluorescence in ultraviolet light, and were chromatographed on a column of alumina (150 g.; Peter Spence and Sons, Ltd., Type H). Elution with light petroleum (b. p. 40—60°) and light petroleum–benzene (9 : 1) afforded on evaporation a pale blue-fluorescing oil (1·69 g.), n_D^{23} 1·5682, part of which was distilled in a bulb tube, having b. p. 140° (bath temp.)/18 mm., n_D^{23} 1·5702, $\lambda_{max.}$ 270 mμ (log ε 3·25). The distilled material rapidly showed an increase in viscosity and became yellow, and satisfactory analytical figures were only obtained on a sample regenerated from the picrate and then distilled (Found: C, 82·2; H, 7·4; MeO, 19·8. $C_{11}H_{12}O$ requires C, 82·5; H, 7·6; 1MeO, 19·4%). The analysis and the ultraviolet light absorption showed the substance to be 1 : 4-*dihydro*-5-*methoxynaphthalene* (XIII). The crude product readily formed a rather unstable *picrate*, which separated from concentrated alcoholic solution in orange-red needles, m. p. 115—116° (Found: C, 52·1; H, 3·9; N, 10·8. $C_{11}H_{12}O,C_6H_3O_7N_3$ requires C, 52·5; H, 3·9; N, 10·8%).

Dehydrogenation of the dihydromethoxynaphthalene (XIII) (0·5 g.) in boiling propionic acid (20 c.c.) with chloranil (0·85 g., 1·1 equiv.) for 6 hr., followed by dilution with ether, washing with excess of alkaline sodium dithionite solution and evaporation of the ether afforded an oil, b. p. 140—143° (bath temp.)/19 mm., n_D^{23} 1·6214, having an infrared absorption spectrum identical with that of methyl α-naphthyl ether, and giving a picrate, m. p. 128—129°, identical with that of methyl α-naphthyl ether.

cis-syn-1 : 4 : 5 : 8 : 9 : 10-*Hexahydro*-1 : 4-*dioxo*-5-*phenylnaphthalene* (XV).—A mixture of 1-phenyl-1 : 3-butadiene [10] (24·35 g.) and methanol (250 c.c.) was stirred and treated with *p*-benzoquinone (19 g.), added in portions. After dissolution was complete the mixture was kept at room temperature for a few hours, diluted with water (25 c.c.), and set aside overnight, a crystalline mass separating. Filtration afforded *cis-syn*-1 : 4 : 5 : 8 : 9 : 10-hexahydro-1 : 4-dioxo-5-phenylnaphthalene (XV) (30·45 g.), sufficiently pure for further use. Crystallisation from light petroleum afforded pale yellow plates, m. p. 100—102° (Found: C, 80·3; H, 6·0. Calc. for $C_{16}H_{14}O_2$: C, 80·6; H, 5·9%). Braude, Jones, and Stern [5] record m. p. 101°.

cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-5-*phenylnaphthalene* (IX; R = H).—The above *cis*-hexahydro-diketone (XV) (30·4 g.) in glacial acetic acid (300 c.c.) was treated at room temperature with zinc powder (30 g.), added in portions with shaking and cooling under running water during 5 min. A further quantity (30 g.) of zinc powder was then added in one

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[10] *Org. Synth.*, 1950, **30**, 75.

lot and shaking was continued for a further 5 min. After filtration and washing of the residue with benzene the filtrate was poured into water and extracted twice with benzene. The combined benzene layers were washed free from acetic acid, concentrated to small bulk under reduced pressure, and diluted with two volumes of light petroleum, affording cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-1 : 4-*dioxo*-5-*phenylnaphthalene* (IX; R = H) in the form of rods (26·7 g.), m. p. 139—140° (Found: C, 80·0; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). The ultraviolet light absorption spectrum showed a series of maxima in the region 255—265 mμ (log ε *ca.* 2·65), indicating that the remaining olefinic linkage was in the 6 : 7-position and not conjugated with the 5-phenyl group.

Stereochemical Equilibration of cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-5-*phenylnaphthalene* (IX; R = H).—(*a*) A solution of the *cis-syn*-diketone (IX; R = H) (2·0 g.) in alcohol-free chloroform (80 c.c.) was saturated with dry hydrogen chloride at 0°. After the addition of methanol (2 c.c.) the solution was kept at room temperature overnight and was then worked up in the usual way. Crystallisation of the solid residue from methanol afforded a *stereoisomer* (XVI) of (IX; R = H) in the form of stout needles, m. p. 124—126° (Found: C, 79·6; H, 6·9. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%), $\lambda_{max.}$ 260, 292 mμ (log ε 2·39 and 1·83 respectively). (*b*) Passage of a solution of the *cis*-diketone (IX; R = H) (1·0 g.) in benzene–light petroleum (b. p. 40—60°) (1 : 1) down a column of activated alumina (20 g.) gave, on further elution with benzene and evaporation of the eluate, a solid residue (1·0 g.), which after several crystallisations from methanol, again gave the diketone (XVI) (0·31 g.), m. p. 124—125°, stereoisomeric with (IX; R = H).

Action of Hydrogen Chloride and Methanol in Chloroform on cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-5-*phenylnaphthalene* (IX; R = H).—A solution of the *cis-syn*-diketone (IX; R = H) (10 g.) in alcohol-free chloroform (200 c.c.) was cooled in ice and saturated with dry hydrogen chloride. Methanol (10 c.c.) was added to the pale yellow solution, and the mixture was kept at room temperature for 65 hr. The then dark solution was worked up in the usual way and a solution of the residual oil in methanol (15 c.c.) was set aside to allow crystallisation to take place. The solid which separated was washed with methanol by decantation, and the combined mother-liquors and washings gave on concentration two further crops of solid. The three crops were combined (A). The final mother-liquor (B) was retained and examined as described below.

The solid (A), on further crystallisation from methanol, gave a mixture of needles and nodules, which were separated by hand. The needles, after several recrystallisations from methanol, afforded the diketone (XVI) (1·6 g.), m. p. 124—126°, stereoisomeric with (IX; R = H). The nodules, after several recrystallisations from methanol, gave a *dimethyl ketal* (XVII) as stout rods (0·82 g.), m. p. 123—124°, depressed to 100—105° on admixture with (XVI) (Found: C, 75·8; H, 7·8; MeO, 20·6. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·7; 2MeO, 21·7%), $\lambda_{max.}$ 261, 290 mμ (log ε 2·43 and 1·68 respectively). The infrared absorption spectrum showed a strong carbonyl-stretching band at 1710 cm.$^{-1}$.

The mother-liquors (B) were taken to dryness, giving a gum (6·32 g.) which was extracted repeatedly by dissolution in small volumes of benzene and addition of 9 volumes of light petroleum (b. p. 40—60°) until a small residue (0·22 g.) remained. The combined 9 : 1 petroleum–benzene extracts (500 c.c.) were allowed to percolate down a column of activated alumina (150 g.; Peter Spence and Sons, Ltd., Type H), and elution was continued with the same solvent mixture until a pale blue-fluorescing band (observed in ultraviolet light) had passed through. Evaporation of the eluate gave a fluorescent oil (1·64 g.), and crystallisation from methanol afforded 1 : 4-*dihydro*-8-*methoxy*-1-*phenylnaphthalene* (XIX) as needles (0·8 g.), m. p. 104—106° (Found: C, 86·6; H, 7·1; MeO, 12·5. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8; 1MeO, 13·0%), $\lambda_{max.}$ 272, 279 mμ in hexane (log ε 3·32 and 3·31 respectively). Dehydrogenation of a sample in boiling anisole with chloranil (2·5 equiv.) for 18 hr., followed by dilution with benzene, washing with excess of alkaline sodium dithionite solution, and evaporation of the solvent, gave a dark oil. When the oil was treated with saturated alcoholic picric acid, a red picrate separated. This dissociated readily on recrystallisation, but a specimen was crystallised successfully from a small volume of methanol to give the *picrate* of 1-methoxy-8-phenylnaphthalene (XVIII) as red needles, m. p. 119° (Found: C, 59·9; H, 3·9; N, 8·9. $C_{17}H_{14}O,C_6H_3O_7N_3$ requires C, 59·6; H, 3·7; N, 9·1%). Regeneration from the picrate afforded a solid, m. p. 47—51°, which, on recrystallisation from methanol, gave 1-*methoxy*-8-*phenylnaphthalene* (XVIII) as tabular prisms, m. p. 55—56° (Found: C, 87·2; H, 6·1; MeO, 13·5. $C_{17}H_{14}O$ requires C, 87·1; H, 6·0;

1MeO, 13·2%), $\lambda_{max.}$ 300, 326 mμ in hexane (log ε 3·89 and 3·54 respectively) (Fig. 1); fine structure bands were at 240, 287, 303, 308, 312, 315, 318, and 326 (vs) mμ.

Continued elution of the chromatogram with benzene–light petroleum (1 : 1) brought off a narrow bright blue-fluorescing band, and evaporation and crystallisation of the residue from methanol afforded 1 : 4-*dihydro*-5 : 8-*dimethoxy*-1-*phenylnaphthalene* (XX) as plates (0·35 g.), m. p. 108—110° (Found; C, 81·1; H, 7·0; MeO, 22·5. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8; 2MeO, 23·3%), $\lambda_{max.}$ 288, 293 mμ (log ε 3·60 and 3·58 respectively).

Elution with benzene and then with chloroform brought off the dimethyl ketal (XVII) (0·8 g.), followed by the diketone (XVI) (1·27 g.), stereoisomeric with the starting material. Strongly adsorbed material (*ca.* 1·4 g.) remained on the alumina as a brown band.

Action of Hydrogen Chloride and Methanol on cis-syn-1 : 4 : 5 : 8 : 9 : 10-*Hexahydro*-1 : 4-*dioxo*-5-*phenylnaphthalene* (XV), *and Preparation of* 1 : 4-*Dihydro*-5 : 8-*dimethoxy*-1-*phenylnaphthalene* (XX).—A solution of the *cis-syn*-hexahydro-diketone (1·0 g.) in alcohol-free chloroform (40 c.c.) was saturated with dry hydrogen chloride at 0°. After the addition of methanol (5 c.c.) the solution was kept at room temperature for 6 days. The solution was then washed successively with water (twice), 2N-sodium hydroxide containing a little sodium dithionite, and water, and evaporated to a tar (0·14 g.). Chromatography of this residue on alumina showed that only strongly adsorbed material was present, and no evidence of a readily eluted fluorescent product was obtained.

Acidification of the alkaline washings with dilute hydrochloric acid gave a buff precipitate, which was collected, washed with water, and dried. Crystallisation from benzene afforded 1 : 4-*dihydro*-5 : 8-*dihydroxy*-1-*phenylnaphthalene* (XXI) as needles (0·5 g.), m. p. 168—169° (Found: C, 80·7; H, 6·4. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%). Methylation with dimethyl sulphate and alkali in methanol solution gave a brown powdery solid, which, on recrystallisation from methanol, afforded the ether (XX), m. p. 110—111°, identical with that obtained above.

1-*Methoxy*-5-*phenylnaphthalene* (cf. Baddar and El-Assal [11]).—5-Methoxy-1-tetralone [12] (3 g.) in ether (50 c.c.) was added to a boiling solution of phenylmagnesium bromide (from 0·8 g. of magnesium and 5·3 g. of bromobenzene) in ether (25 c.c.). After being heated under reflux for ½ hr., the mixture was cooled and decomposed with ice and dilute sulphuric acid. Evaporation of the ethereal solution gave an oil (4·32 g.) which was taken up in light petroleum (b. p. 40—60°) and allowed to percolate down a column of alumina (60 g.). Elution with the same solvent afforded a colourless oil (2·11 g.), which was freed from traces of diphenyl by steam-distillation. The resulting 1 : 2-dihydro-8-methoxy-4-phenylnaphthalene failed to crystallise, although Baddar and El-Assal [11] report m. p. 47—48°. Part (0·5 g.) of the product was dehydrogenated by heating it with chloranil (1·25 g., 2 equiv.) for 18 hr. in boiling anisole (25 c.c.). Working up as described above afforded 1-methoxy-5-phenylnaphthalene as leaflets, m. p. 81—82°; Baddar and El-Assal [11] report m. p. 84—85°. Ultraviolet light absorption max. in hexane were at 222, 235 (infl.), 299, 322 (infl.) mμ (log ε 4·60, 4·49, 3·99, and 3·77 respectively) (Fig. 1); fine structure bands were at 236, 240, 251, 276, 287, 301 (very broad), 310 (broad), 316, and 324 (vs) mμ.

cis-syn-1 : 4 : 5 : 8 : 9 : 10-*Hexahydro*-5-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene*.—1-*p*-Methoxyphenylbut-2-en-1-ol [5] (5 g.) was heated in benzene (50 c.c.) with a crystal of iodine under reflux with the conventional Dean and Stark apparatus in the presence of a little *N*-phenyl-β-naphthylamine as a polymerisation inhibitor. Evolution of water (0·4 c.c.) ceased after 2 hr. and the benzene solution was cooled and treated with *p*-benzoquinone (3·26 g.). After 65 hr. at room temperature the solution was evaporated to dryness under reduced pressure, and crystallisation of the residue from methanol afforded *cis-syn*-1 : 4 : 5 : 8 : 9 : 10-hexahydro-5-*p*-methoxyphenyl-1 : 4-dioxonaphthalene (4·39 g.), m. p. 97—100°, raised to 106° on recrystallisation from light petroleum (b. p. 80—100°). Braude, Jones, and Stern [5] record m. p. 103°.

cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-5-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (IX; R = MeO).—The *cis-syn*-hexahydro-diketone (6·4 g.) was reduced with zinc powder (2 × 6·4 g.) in glacial acetic acid in the manner described above for similar reductions. Crystallisation of the crude product from benzene–light petroleum afforded cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-5-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (IX; R = MeO) as prisms (4·28 g.), m. p. 113—114° (Found: C, 75·4; H, 6·8. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%), $\lambda_{max.}$ 278 mμ (log ε 3·29).

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[11] Baddar and El-Assal, *J.*, 1951, 1844.

[12] Locket and Short, *J.*, 1939, 787.

Stereochemical Equilibration of cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-5-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (IX; R = MeO).—(*a*) A solution of the *cis-syn*-diketone (IX; R = MeO) (1·0 g.) in alcohol-free chloroform (40 c.c.) was saturated with dry hydrogen chloride at 0°. After 24 hr. at room temperature the product was isolated in the usual way. Several crystallisations from benzene afforded a *stereoisomeric diketone* (XXIIIa) as fine needles, m. p. 164° (Found: C, 75·8; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%), $\lambda_{max.}$ 278 mμ (log ε 3·22). The mother-liquors afforded a third *stereoisomeric diketone* (XXIIIb) as needles, m. p. 135—136° (Found: C, 75·5; H, 6·7%), $\lambda_{max.}$ 278 mμ (log ε 3·23). (*b*) A similar mixture of the two stereoisomers (XXIIIa and b) was obtained when a solution of the *cis-syn*-diketone (IX; R = MeO) in benzene–light petroleum was passed down a column of alkaline activated alumina, followed by elution with benzene.

Action of Hydrogen Chloride and Methanol in Chloroform on cis-syn-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-5-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (IX; R = MeO).—(a) *For* 24 *hr.* A solution of the *cis-syn*-diketone (1·0 g.) in alcohol-free chloroform (40 c.c.) was saturated with dry hydrogen chloride at 0°, and methanol (2 c.c.) was then added. After 24 hr. the solution was worked up in the usual way. Several recrystallisations of the product from benzene–light petroleum gave the stereoisomeric diketone (XXIIIb) (0·52 g.), m. p. 135—136°, identical with that obtained as above. Chromatography of the material recovered from the mother-liquors, in benzene–light petroleum (b. p. 40—60°) (1 : 1) solution on a column of alumina (20 g.), gave a readily eluted fraction, crystallising from methanol to give 1 : 4-*dihydro*-8-*methoxy*-1-p-*methoxyphenylnaphthalene* (XXIV) as needles (70 mg.), m. p. 123—124° (Found: C, 81·1; H, 6·5; MeO, 23·3. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8; 2MeO, 23·3%), $\lambda_{max.}$ 275 (infl.), 279, 283 (infl.) mμ in hexane (log ε 3·51, 3·57, and 3·34 respectively). Further elution of the column gave a small quantity (100 mg.) of the high-melting stereoisomer (XXIIIa), m. p. 159—160°, identical with that obtained previously.

Dehydrogenation of 1 : 4-dihydro-8-methoxy-1-*p*-methoxyphenylnaphthalene (XXIV) (0·5 g.) in boiling anisole with chloranil (1·02 g.; 2·2 equiv.) for 21 hr., followed by the usual method of working-up, afforded a semi-solid tar. This was purified by percolation in benzene–light petroleum (1 : 1) down a column of alumina (15 g.). Elution with the same solvent (250 c.c.) and evaporation left a solid (0·38 g.), which, on crystallisation from methanol, afforded 1-*methoxy*-8-p-*methoxyphenylnaphthalene* (XXV) as laths, m. p. 77° (Found: C, 81·7; H, 5·9; MeO, 23·0. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; 2MeO, 23·5%), $\lambda_{max.}$ 234, 301, 325 mμ in hexane (log ε 4·65, 4·05 and 3·76 respectively) (Fig. 2); fine structure bands were at 288, 301, 306, 314, 322, and 326 mμ. The free phenol, obtained in a qualitative demethylation experiment by using hydrogen iodide and acetic anhydride, gave a deep blue colour with Gibbs's reagent.[7]

(b) *For* 72 *hr.* A solution of the *cis-syn*-diketone (IX; R = MeO) (10 g.) in alcohol-free chloroform (200 c.c.) was saturated with hydrogen chloride at 0°, then treated with methanol (10 c.c.) and set aside for 72 hr. at room temperature. Working up in the usual way gave a semi-solid residue, which was taken up in methanol–benzene and allowed to crystallise. The resulting solid (4·20 g.), after several crystallisations from benzene–light petroleum afforded the diketone (XXIIIa) (2·03 g.), m. p. 164°. The first mother-liquor from the recrystallisation of this substance gave, on concentration, clusters of stout prisms, which, after several further recrystallisations from benzene–light petroleum, afforded 1 : 4-dihydro-8-methoxy-1-*p*-methoxyphenylnaphthalene (XXIV) (0·78 g.), m. p. 123—124°, identical with that described in (a).

The original methanol–benzene mother-liquors were taken to dryness and the residue was extracted repeatedly with light petroleum (b. p. 40—60°)–benzene (9 : 1) until a small insoluble residue (0·7 g.) remained. The combined extracts (450 c.c.) were allowed to percolate down a column of alumina (150 g.), and elution with light petroleum–benzene (4 : 1) afforded a further quantity (0·31 g.) of 1 : 4-dihydro-8-methoxy-1-*p*-methoxyphenylnaphthalene (XXIV); the mother-liquors from this gave amorphous material and needles on storage, and, after hand-sorting, several recrystallisations of the latter from methanol gave a *substance* as needles, m. p. 76—76·5° (Found: C, 77·7, 77·9; H, 6·4, 6·7; MeO, 19·6, 22·2. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5; 2MeO, 20·1%), $\lambda_{max.}$ 275 (infl.), 280, 285 (infl.) (log ε 3·58, 3·64, and 3·44 respectively). Dehydrogenation of this substance (29 mg.) with chloranil (100 mg.) in anisole in the usual way afforded 1-methoxy-5-*p*-methoxyphenylnaphthalene (XXVI), identical (m. p., mixed m. p., and infrared absorption spectrum) with an authentic specimen (below).

Further elution of the column with benzene afforded a mixture, which was resolved into two components by crystallisation from benzene–light petroleum and hand-sorting. The minor component, m. p. 161—163°, was the high-melting stereoisomeric diketone (XXIIIa); the other component crystallised from benzene–light petroleum in prisms (1·0 g.) and was a *dimethyl ketal* (XXVII), m. p. 132—133° (Found: C, 72·5; H, 7·7; MeO, 29·4. $C_{19}H_{24}O_4$ requires C, 72·1; H, 7·6; 3MeO, 29·4%).

The ketal (XXVII) (0·12 g.) was dissolved in a few drops of warm acetic acid, and the solution was diluted with water and set aside to allow crystallisation to occur. The solid product was collected and crystallisation from benzene–light petroleum afforded a fourth stereoisomeric 1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*octahydro*-5-p-*methoxyphenyl*-1 : 4-*dioxonaphthalene* (XXIIIc) in the form of needles, m. p. 155—156°, depressed to below 135° on admixture with the stereoisomer (XXIIIa) of m. p. 164° (Found: C, 75·5; H, 6·6. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%) and with ultraviolet light absorption max. at 277, 285 mμ (log ε 3·27 and 3·17 respectively).

1-*Methoxy*-5-p-*methoxyphenylnaphthalene* (XXVI).—5-Methoxy-1-tetralone [12] (3·0 g.) in ether (30 c.c.) was added dropwise to a boiling solution of *p*-methoxyphenylmagnesium bromide (from 0·83 g. of magnesium and 6·4 g. of *p*-bromoanisole) in ether (30 c.c.). After 1 hr. under reflux the mixture was cooled and decomposed with ice and dilute sulphuric acid. The organic layer was separated, washed with dilute sulphuric acid and then with water, dried, and evaporated. The residue was distilled in steam for 1½ hr., the distillate being rejected, and again recovered as a crystalline solid. Recrystallisation from methanol–benzene afforded 1 : 2-*dihydro*-8-*methoxy*-4-p-*methoxyphenylnaphthalene* as laths (1·95 g.), m. p. 125—126° (Found: C, 81·2; H, 7·1; MeO, 22·7. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8; 2MeO, 23·3%), $\lambda_{max.}$ 222, 273 mμ (log ε 4·57 and 4·02 respectively).

The dihydro-compound (0·5 g.) was dehydrogenated with chloranil (0·51 g.; 1·1 equiv.) in boiling anisole (25 c.c.) for 6 hr., and the product was isolated in the usual manner. Crystallisation from benzene–light petroleum afforded 1-*methoxy*-5-p-*methoxyphenylnaphthalene* (XXVI) as plates (0·42 g.), m. p. 130—131° (Found: C, 82·0; H, 5·9; MeO, 23·6. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1; 2MeO, 23·5%), $\lambda_{max.}$ 231, 301, 322 (infl.) mμ in hexane (log ε 4·62, 4·06, and 3·81 respectively) (Fig. 2); fine structure bands were at 284·5, 301·5, 311, 316·5, and 324 mμ.

Action of Hydrogen Chloride and Methanol in Chloroform on cis-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-*Octahydro*-1 : 4-*dioxo*-6-*phenylnaphthalene* (VII; R = H).—A solution of the *cis*-diketone (VII; R = H) (9·0 g.) in alcohol-free chloroform (150 c.c.) was cooled in ice, saturated with dry hydrogen chloride, treated with methanol (9 c.c., *ca.* 10 equiv.), and then kept at room temperature for 64 hr. The mixture was worked up in the usual way, and crystallisation of the crude oily product from methanol–benzene gave 1 : 2-dihydro-8-methoxy-3-phenylnaphthalene (XXIX) (1·46 g.), m. p. 81—83°, identical with that previously isolated (Part II). The material recovered from the mother-liquor was extracted several times, with benzene–light petroleum (b. p. 40—60°) (1 : 9), the final tarry residue (2·0 g.) being rejected. The combined extracts were allowed to percolate down a column of alumina (80 g.) which was eluted with the same solvent mixture. Evaporation of the eluate (1 l.) gave a colourless oil (2·48 g.), showing a strong blue fluorescence in sunlight or ultraviolet light. The column was not further investigated.

Crystallisation of the fluorescent oil from methanol–benzene afforded a further quantity (0·83 g.) of 1 : 2-dihydro-8-methoxy-3-phenylnaphthalene (XXIX). The material from the mother-liquor was dissolved in a little light petroleum; when the solution was stored at 2° for 24 hr., nodules (1·11 g.) separated (m. p. 45—65°). Repeated crystallisation of the solid from light petroleum (b. p. 40—60°), combined with hand-sorting when practicable, afforded a still further quantity (0·26 g.) of the dihydro-compound (XXIX) and another component (XXXI), which crystallised from light petroleum (b. p. 40—60°) in nodular prisms (0·58 g.), m. p. 59—60° (Found: C, 86·6, 86·7; H, 6·8, 6·9; MeO, 12·6. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8; 1MeO, 13·0%), $\lambda_{max.}$ 240, 312—322 (flat plateau) mμ in hexane (log ε 4·19 and 4·21 respectively). The infrared absorption spectrum in CCl_4 resembled in general, but showed significant variation from, that of authentic 1 : 2-dihydro-5-methoxy-3-phenylnaphthalene (XXXI), prepared as described below.

Dehydrogenation of this material, m. p. 59—60° (0·11 g.), with chloranil (0·23 g.; 2 equiv.) in boiling anisole for 16 hr. and isolation of the product in the usual way afforded, on crystallisation from methanol–benzene, 1-methoxy-7-phenylnaphthalene (XXX) as prisms (70 mg.), m. p. 67—68°, identical with an authentic specimen prepared as described below.

1 : 7-*Dimethoxynaphthalene* (XXXII).—Technical 1 : 7-dihydroxynaphthalene (50 g.), dissolved in water (220 c.c.) containing sodium hydroxide (29 g.), was methylated at *ca.* 70°

under nitrogen by the dropwise addition of dimethyl sulphate (63 g.) with vigorous stirring. After dilution with water and extraction with ether, the ether layer was washed with water, 2N-sodium hydroxide, and water, then dried and fractionated to give 1 : 7-*dimethoxynaphthalene* (17·6 g.), b. p. 123—130°/0·4 mm., n_D^{22} 1·6208 (Found: C, 77·0; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

8-*Methoxy*-2-*tetralone* (XXXIII).—1 : 7-Dimethoxynaphthalene (10·4 g.) was reduced in boiling butan-1-ol (250 c.c.) by the addition of sodium (20 g.) in pieces as rapidly as possible. When all the sodium had dissolved (1½ hr.), water (200 c.c.) and concentrated hydrochloric acid (200 c.c.) were added, and the mixture was heated on the steam-bath for ½ hr. with frequent shaking. The butanol was removed by steam-distillation and the crude product was recovered in ether, washed, and dried. The concentrated ethereal solution was shaken for 18 hr. with freshly prepared saturated sodium hydrogen sulphite solution (50 c.c.). The resulting bisulphite compound was collected, washed with ether, and decomposed in aqueous suspension with excess of sodium carbonate. Extraction with ether gave a solid (3·8 g.), and crystallisation from light petroleum (b. p. 40—60°) gave 8-*methoxy*-2-*tetralone* as needles, m. p. 58—59° (Found: C, 75·0; H, 7·1. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%).

1 : 2-*Dihydro*-5-*methoxy*-3-*phenylnaphthalene* (XXXI).—8-Methoxy-2-tetralone (1·5 g.) in ether (25 c.c.) was added to an ice-cold ether solution of phenylmagnesium bromide (from 0·63 g. of magnesium and 4·0 g. of bromobenzene), and the mixture was then heated under reflux for ½ hr. After cooling and decomposition with ice and dilute sulphuric acid, the ether layer was separated, washed, dried, and evaporated. The residue was freed from traces of diphenyl by steam-distillation, and the product was again recovered in ether. The resulting yellow oil (1·63 g.) was heated under reflux for 45 min. with anhydrous formic acid (20 c.c.), and the mixture was diluted with water and extracted with ether. The residue from the washed ethereal solution was allowed to percolate in benzene–light petroleum (b. p. 40—60°) (1 : 9) through a column of activated alumina (30 g.) and the blue-fluorescing band was eluted with benzene–light petroleum (1 : 9). The solid (1·1 g.) left on evaporation of the eluate (400 c.c.) was crystallised from light petroleum, to give 1 : 2-*dihydro*-5-*methoxy*-3-*phenylnaphthalene* (XXXI) as prisms, m. p. 51—52° (Found: C, 86·3; H, 6·7; MeO, 13·3. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8; MeO, 13·0%), $\lambda_{max.}$ 235, 317 (infl.), 324 mμ with a broad flattened area in the range 315—328 mμ (log ε 4·22, 4·37, and 4·38 respectively).

1-*Methoxy*-7-*phenylnaphthalene* (XXX).—1 : 2-Dihydro-5-methoxy-3-phenylnaphthalene (0·2 g.) was dehydrogenated with chloranil (0·5 g., 2 equiv.) in boiling anisole for 22 hr. The mixture was worked up in the usual way, and the solid residue, crystallised from benzene–methanol, afforded 1-*methoxy*-7-*phenylnaphthalene* as prisms (0·16 g.), m. p. 67—68°, identical with the substance described above (Found: C, 87·0; H, 6·3; MeO, 13·5. $C_{17}H_{14}O$ requires C, 87·1; H, 6·0; MeO, 13·2%). Its ultraviolet light absorption max. in hexane were at 254, 303 mμ (log ε 4·72 and 3·97 respectively). The identity of this substance with that obtained above was confirmed by comparison of the infrared absorption spectra of the two substances.

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National Institute for Medical Research,
The Ridgeway, Mill Hill, London, N.W.7.

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