*The Synthesis of Potential Androgens. Part II.**

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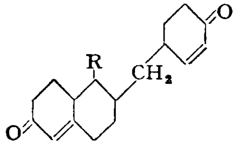
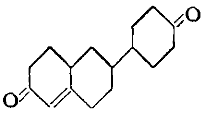
Substances bearing a superficial resemblance to testosterone have been synthesised for androgenic testing. In addition anisoin and anisil have been submitted to the sodium and liquid ammonia reduction.

Following from the work described in Part I * it was decided to prepare several diketones of the general type (I), which are dehydrogenated homologues of the compound (II) reported by Wilds and Shunk (*J. Amer. Chem. Soc.*, 1949, **71**, 3266) to be feebly androgenic.

Condensation of 6-methoxy-1-tetralone with *p*-methoxybenzaldehyde gave a good yield of the αβ-unsaturated ketone, which was catalytically reduced to the benzyl compound (III). Clemmensen reduction of the latter failed, but reduction by Huang-Minlon's method afforded the ether (IV; R = H). This was sparingly soluble in a mixture of liquid ammonia and ethanol, but reduction was effected under the conditions found to be the most suitable for this type of reaction, *viz.*, by using an approximately 50% mixture of liquid ammonia and ethanol; in this mixture sodium does not dissolve to give a blue solution, nor does it remain solid metal, as when it is added to ethanol; instead, a copper-coloured molten mass is formed, and this dissolves slowly and quietly as the reduction proceeds. The yields by this technique were greatly superior to those obtained by using less alcohol. In this way the benzyl compound (IV; R = H) was reduced to a compound that on hydrolysis yielded the αβ-unsaturated ketone (I; R = H) (the intermediate βγ-unsaturated ketone was not isolated).



(I)



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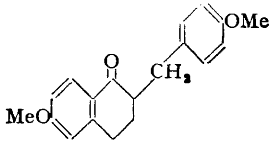

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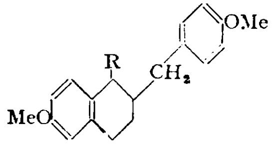

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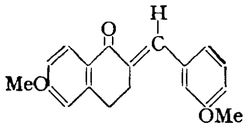

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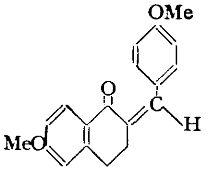

(VI)

Repetition of this series of reactions with *m*-methoxybenzaldehyde afforded, on two different occasions, two different αβ-unsaturated ketones in the first step. These were shown to be chemical individuals not polymorphs and must be *cis–trans*-isomers: in agreement, both substances yielded the same dihydro-derivative on catalytic hydrogenation. The αβ-unsaturated ketones produced in the initial condensations of 6-methoxy-1-tetralone with *o*-, *m*-, and *p*-methoxybenzaldehyde form 2 : 4-dinitrophenylhydrazones only with difficulty, whereas the reduced ketones form these derivatives with ease. It is suggested that this difficulty of hydrazone formation in the unsaturated bodies is a result of steric hindrance, and that these compounds have the *cis*-configuration as in (VI). Of the two isomers obtained in the *m*-methoxy-series that formed as in the *o*- and *p*-series by allowing the reaction mixture to cool until separation of the ketone occurs is presumably the *cis*-form analogous to (VI), whilst the isomer obtained by pouring the mixture into water and isolating and distilling the product probably has the *trans*-configuration (V).

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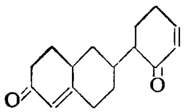
* Part I, preceding paper.

Insufficient quantities of *m*-methoxybenzaldehyde were available to permit extension of this series of reactions beyond the dihydro-derivative of (V).

The sequence of reactions was carried through with *o*-methoxybenzaldehyde to the diketone (VII). An attempt to reduce the double bond of the benzylidene-ketone (VIII) and the carbonyl group (to CH_2) in one reaction catalytically in acetic acid and perchloric acid over palladised charcoal (cf. Rosenmund and King, *Ber.*, 1942, **75**, 1850; Hornung and Reisner, *J. Amer. Chem. Soc.*, 1948, **70**, 3619; 1949, **71**, 1036) gave only the saturated alcohol (IX).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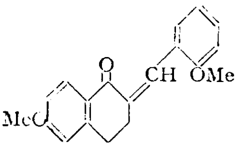
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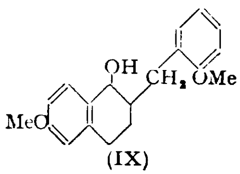
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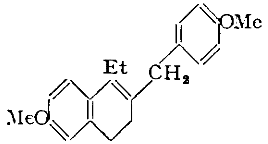
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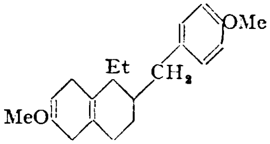
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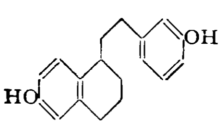
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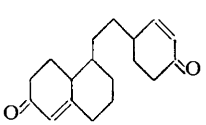
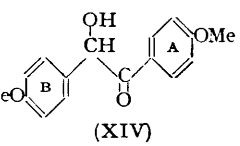

(XIII)

Condensation of (III) with ethylmagnesium iodide and dehydration of the product by distillation afforded 1-ethyl-3 : 4-dihydro-6-methoxy-2-4′-methoxybenzylnaphthalene (X), hydrogenation of which yielded the ether (IV; R = Et). Reduction of the latter with sodium, ammonia, and ethanol under the conditions outlined above gave excellent yields of the enol ether (XI), and thence by hydrolysis the αβ-unsaturated diketone (I; R = Et).

As the diphenol (XII) is oestrogenic (Buchta, Galster, and Dauner, *Chem. Ber.*, 1949, 82, 207) a reduced analogue was prepared for androgenic testing. Interaction of 6-methoxy-1-tetralone and 2-(*p*-methoxyphenyl)ethylmagnesium bromide afforded 3 : 4-dihydro-4-methoxy-1-(2-4′-methoxyphenylethyl)naphthalene, reduction of which gave the corresponding tetrahydronaphthalene. As this was too sparingly soluble for reduction with sodium, ammonia, and ethanol, it was demethylated and converted into the 2-hydroxyethyl ether, which was then reduced as before, and the product was hydrolysed to the αβ-unsaturated ketone (XIII).

The compounds (I; R = H and Et), (VII), and (XIII) were all androgenically inactive, and this series of investigations was finally abandoned.

During these investigations the reduction of anisoin with sodium and liquid ammonia was carried out as a preliminary to preparation of analogues of the hexane (XV; R = R′ = Et) obtained by Birch and Mukherji (*J.*, 1949, 2531) from hexoestrol.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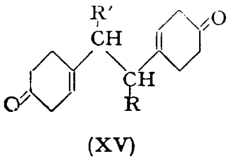
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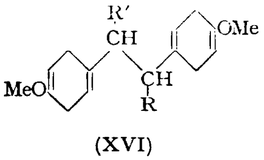
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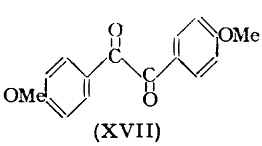
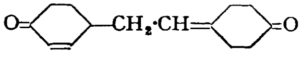

(XVII)

The reduction proceeded readily and gave two substances (XVI; R = OH, R′ = H; R = R′ = H). These probably arise as follows. The nucleus A of anisoin (XIV) having a CO substituent would be rapidly reduced, whereas nucleus B would be reduced more slowly, and indeed the hydrogenolysis of the benzyl-alcoholic hydroxyl group must precede the reduction of B. The reduction of the carbonyl group will compete with the reduction of nucleus A as the first process, and when this reduction precedes nuclear reduction both rings will become identical and elimination of both central oxygen functions will occur; when, however, nuclear reduction precedes reduction of the carbonyl group the reduction of the latter will not give a benzyl alcohol and retention of the alcoholic OH group would be expected, giving (XVI; R = OH, R′ = H). As expected from this theory, anisil (XVII), when reduced in the same way, gave the diol (XVI; R = R′ = OH).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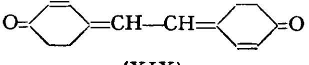
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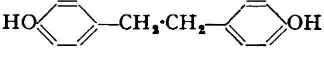
(XX)

The hydrolysis of these derivatives of anisoin and anisil gave rise to interesting compounds. The hydrolysis of the alcohol (XVI; R = OH, R′ = H) apparently involves simultaneous dehydration, presumably giving the conjugated unsaturated ketone (XVIII). Double dehydration also appears to accompany the hydrolysis of the diol (XVI; R = R′ = OH), giving the highly unsaturated ketone (XIX). The isomeric dihydroxydiphenylethane structure (XX) for this substance was eliminated by the melting point, the ultraviolet absorption spectrum, and the formation of a 2 : 4-dinitrophenylhydrazone. The ketone rapidly degenerates into tars.

EXPERIMENTAL

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-2-4′-*methoxybenzylidene*-1-*oxonaphthalene*.—A solution of sodium (2 g.) in ethanol (50 ml.) was added to one of 6-methoxy-1-tetralone (15 g.) and *p*-methoxybenzaldehyde (18 g.) in ethanol (100 ml.) at 75° in a 200-ml. flask with exclusion of air. On slow cooling, pale yellow plates separated. These were collected, washed with cold ethanol, and recrystallised from 500 ml. of ethanol, yielding the *methoxybenzylidene derivative* as pale yellow, irregular plates, m. p. 139·5° (Found: C, 77·4; H, 6·1. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·1%), which gave a 2 : 4-dinitrophenylhydrazone only with great difficulty.

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-2-4′-*methoxybenzyl*-1-*oxonaphthalene*.—The foregoing product (15 g.) in purified dioxan (170 ml.) was shaken under hydrogen in the presence of palladised strontium carbonate. Hydrogen was steadily absorbed and reaction was stopped when one mol. had been absorbed (1143 ml. at N.T.P.). The catalyst was removed and the mixture concentrated under reduced pressure and poured into water. An oil which separated solidified and recrystallised from ethanol, giving the *benzyl compound* as prisms, m. p. 94° (Found: C, 76·7; H, 6·6. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·7%). The 2 : 4-*dinitrophenylhydrazone* formed dark red needles, m. p. 210°, from Cellosolve (2-ethoxyethanol) (Found: C, 63·0; H, 4·9; N, 11·7. $C_{25}H_{24}O_6N_4$ requires C, 63·2; H, 5·0; N, 11·7%).

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-2-4′-*methoxybenzylnaphthalene*.—(*a*) 1 : 2 : 3 : 4-Tetrahydro-6-methoxy-2-4′-methoxybenzyl-1-oxonaphthalene (10 g.) was recovered after 48 hours' boiling with toluene (100 ml.), amalgamated zinc (100 g.), and concentrated hydrochloric acid (350 ml.), almost completely unchanged. (*b*) 1 : 2 : 3 : 4-Tetrahydro-6-methoxy-2-4′-methoxybenzyl-1-oxonaphthalene (15 g.) and 100% hydrazine hydrate (5 ml.) were boiled with a solution of sodium (5 g.) in diethylene glycol (150 ml.) for 1 hr. Water was then allowed to distil until the b. p. reached 200°, and the mixture was boiled under reflux, in an atmosphere of nitrogen, for 6 hr. No precipitate was obtained when the mixture was poured into water (500 ml.), so the phenol was remethylated immediately by the addition of sodium hydroxide (20 g.) and, slowly, methyl sulphate (50 ml.), with stirring and heating. Cooling, dilution with water (750 ml.), ether-extraction, evaporation, and distillation gave 1 : 2 : 3 : 4-*tetrahydro*-6-*methoxy*-2-4′-*methoxybenzylnaphthalene*, b. p. 185°/0·2 mm. (Found: C, 81·1; H, 8·1. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·8%). This compound was non-ketonic and non-phenolic.

1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*Octahydro*-6-*oxo*-2-(4-*oxo*cyclo*hex*-2-*enylmethyl*)*naphthalene*.—1 : 2 : 3 : 4-Tetrahydro-6-methoxy-2-4′-methoxybenzylnaphthalene (15 g.) in ethanol (500 ml.) was added, followed by sodium (20 g.) in slices, to liquid ammonia (500 ml.), with vigorous stirring until dissolution of the sodium was complete, then the whole was poured into water (1000 ml.) and extracted with ether, and the extracts were evaporated. The residual oil was warmed at 40° with alcoholic 2N-hydrochloric acid for 10 min., and the mixture poured into water and extracted with ether. The ether extract was shaken for 10 hr. with saturated aqueous sodium hydrogen sulphite, and the bisulphite compound collected and washed with ether. The ketone recovered from the bisulphite compound by decomposition and extraction with ether was heated at 50° for 5 min. with alcoholic sodium ethoxide in an atmosphere of nitrogen, the solution poured into dilute acetic acid, and the precipitated oil extracted with ether, which afforded 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydro*-6-*oxo*-2-(4-*oxo*cyclo*hex*-2-*enylmethyl*)*naphthalene*

(I; R = H) as a pale brown oil, b. p. 180°/0·05 mm. (Found: C, 70·5; H, 8·7. $C_{17}H_{22}O_2$ requires C, 79·0; H, 8·5%), $\lambda_{max.}$ 2280 Å (ε 10,000).

1-*Ethyl*-3 : 4-*dihydro*-6-*methoxy*-2-4′-*methoxybenzylnaphthalene* (X).—6-Methoxy-2-4′-methoxybenzyl-1-tetralone (9 g.) and excess of ethylmagnesium iodide [from ethyl iodide (28 g.) and magnesium (5 g.)] in dry benzene (60 ml.) and dry ether (240 ml.) were heated under reflux for 5 hr., then cooled and decomposed by dilute hydrochloric acid and ice. The ether–benzene layer was separated and the aqueous layer extracted once with ether. The combined extracts were shaken with sulphurous acid, then with sodium hydrogen carbonate solution, dried, and evaporated. The residual oil was distilled, to give a pale yellow oil, b. p. 193—195°/0·07 mm., which solidified. On low-temperature recrystallisation from ether 1-*ethyl*-3 : 4-*dihydro*-6-*methoxy*-2-4′-*methoxybenzylnaphthalene* was obtained as needles or prisms, m. p. 49—50° (Found: C, 82·0; H, 7·6. $C_{21}H_{24}O_2$ requires C, 81·8; H, 7·6%).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-6-*methoxy*-2-4′-*methoxybenzylnaphthalene* (IV; R = Et).—A solution of the foregoing dihydronaphthalene (12 g.) in ethanol (200 ml.) was shaken under hydrogen at atmospheric pressure and 50° with palladised strontium carbonate. Absorption of hydrogen (870 ml.) ceased after 2 hr. The *tetrahydronaphthalene* was an almost colourless oil, b. p. 210—215°/0·1 mm. (Found: C, 81·4; H, 8·2. $C_{21}H_{26}O_2$ requires C, 81·3; H, 8·4%).

1-*Ethyl*-1 : 2 : 3 : 4 : 5 : 8-*hexahydro*-6-*methoxy*-2-(4-*methoxy*cyclo*hexa*-1 : 4-*dienylmethyl*)-*naphthalene* (XI).—The preceding product (10·5 g.) in 2-ethoxyethanol (75 ml.) and ethanol (75 ml.) was added to a well-stirred solution of sodium (3 g.) in liquid ammonia (600 ml.), then, gradually, more sodium (total 20 g.) and ethanol (total 500 ml.) until the sodium appeared as a copper-coloured molten mass on the surface of the liquid. Vigorous stirring was then continued until all the sodium had dissolved. The mixture was poured into water and extracted with ether. The extracts yielded an oil (8·5 g.) which when distilled gave the cyclo*hexadienyl compound*, b. p. 170—175/0·04 mm. (Found: C, 80·1; H, 9·6. $C_{21}H_{30}O_2$ requires C, 80·2; H, 9·6%).

1-*Ethyl*-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydro*-6-*oxo*-2-(4-*oxo*cyclo*hex*-2-*enylmethyl*)*naphthalene* (I; R = Et).—A solution of the preceding *cyclo*hexadienyl compound (1·5 g.) in ether (10 ml.) was shaken with 2N-hydrochloric acid (10 ml.) for 5 hr. The ether layer was separated and the aqueous layer saturated with ammonium chloride and extracted with ether. From the ether extracts an oil was obtained and distilled; pale yellow 1-*ethyl*-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydro*-6-*oxo*-2-(4-*oxo*cyclo*hex*-2-*enylmethyl*)*naphthalene* was obtained, having b. p. 165—170°/0·05 mm. (Found: C, 80·2; H, 9·0. $C_{19}H_{26}O_2$ requires C, 79·8; H, 9·1%), $\lambda_{max.}$ 2290 Å (ε 10,009).

6-*Methoxy*-2-2′-*methoxybenzylidene*-1-*tetralone*.—A solution of sodium (1 g.) in ethanol (30 ml.) was added to one of 6-methoxy-1-tetralone (15 g.) and *o*-methoxybenzaldehyde (18 g.) in ethanol (100 ml.) at 75°, with exclusion of air. After long storage crystals separated and on recrystallisation from ethanol gave 6-*methoxy*-2-2′-*methoxybenzylidene*-1-*tetralone* as pale yellow prisms, m. p. 87·5° (Found: C, 78·0; H, 6·2. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1%). The 2 : 4-*dinitrophenylhydrazone* was formed very slowly on the water-bath, and formed bright red prisms, m. p. 182°, from 2-ethoxyethanol (Found: C, 62·8; H, 4·5; N, 11·0. $C_{25}H_{22}O_6N_4$ requires C, 63·2; H, 4·6; N, 11·8%).

6-*Methoxy*-2-2′-*methoxybenzyl*-1-*tetralone*.—A solution of the benzylidenetetralone (10 g.) in purified dioxan (170 ml.) was shaken under hydrogen over palladised strontium carbonate until absorption of hydrogen, at first steady, became markedly slower (762 ml. absorbed). Removal of the catalyst and most of the solvent, pouring into water (200 ml.), extraction with ether, distillation (b. p. 206—209°/0·1 mm.), and low-temperature recrystallisation from ether gave the 2-2′-*methoxybenzyl compound*, prisms, m. p. 68° (Found: C, 76·6; H, 6·5. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·7%). The 2 : 4-*dinitrophenylhydrazone*, formed fairly readily, was bright red prisms, m. p. 176° (from 2-ethoxyethanol) (Found: C, 63·2; H, 5·1; N, 11·9. $C_{25}H_{24}O_6N_4$ requires C, 63·1; H, 5·0; N, 11·8%).

6-*Methoxy*-2-2′-*methoxybenzyl*-1-*tetralol*.—A solution of the 2-2′-methoxybenzylidenetetralone (2 g.) in acetic acid (20 ml.) and 60% perchloric acid (1 ml.) containing palladised charcoal (0·6 g.) was shaken under hydrogen at atmospheric pressure and 55°. When 305 ml. hydrogen had been absorbed (*ca.* 5 hr.) the mixture was freed from catalyst, neutralised, and extracted with ether. The ether extracts yielded a yellow oil that crystallised on trituration with ether. Recrystallisation from ethanol gave the *tetralol*, pale brown prisms, m. p. 82° [Found: C, 76·3; H, 6·8%; *M* (Rast), 318. $C_{19}H_{22}O_3$ requires C, 76·5; 7·3%; *M*, 298].

1 : 2 : 3 : 4-*Tetrahydro*-6-*methoxy*-2-2′-*methoxybenzylnaphthalene*.—6-Methoxy-2-2′-methoxybenzyl-1-tetralone (10 g.) and 100% hydrazine hydrate (5 ml.) were added to a solution of sodium (2·5 g.) in diethylene glycol (75 ml.) and the mixture boiled for 1 hr. Then water was

distilled until the b. p. rose to 200°, whereafter the mixture was refluxed for a further 6 hr., poured into water, and methylated as described for the 4-methoxybenzyl isomer. The product was isolated by ether-extraction and distilled, giving 1 : 2 : 3 : *4-tetrahydro-6-methoxy-2-2′-methoxybenzylnaphthalene*, almost colourless, b. p. 150—155°/0·02 mm. (Found : C, 80·8; H, 8·1. $C_{19}H_{22}O_2$ requires C, 80·8; H, 7·8%).

1 : 2 : 3 : 4 : 5 : *8-Hexahydro-6-methoxy-2-(2-methoxy*cyclo*hexa-*1 : *4-dienylmethyl)naphthalene*.—A solution of the 2-2′-methoxybenzyltetralin (8·5 g.) in ethanol (100 ml.) was added dropwise to a stirred solution of sodium (3 g.) in liquid ammonia (750 ml.), then more sodium (total 18 g.) and ethanol (total 600 ml.). After the sodium had dissolved, the mixture was poured into water. By means of ether, the cyclo*hexadienyl compound* (crude, 7 g.) was obtained as a pale yellow oil, b. p. 158—162°/0·02 mm. (Found : C, 80·0; H, 9·2. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·1%).

1 : 2 : 3 : 4 : 6 : 7 : 8 : *9-Octahydro-6-oxo-2-(2-oxo*cyclo*hex-3-enylmethyl)naphthalene*.—A solution of the preceding product (2 g.) in ether (15 m.) was shaken with 2N-hydrochloric acid (25 ml.) for 5 hr. The ether layer was separated, and the aqueous layer saturated with ammonium chloride and extracted once with ether. The combined ether solutions yielded a pale yellow oil (1·4 g.), which was distilled; 1 : 2 : 3 : 4 : 6 : 7 : 8 : *9-octahydro-6-oxo-2-(2-oxo*cyclo*hex-3-enylmethyl)naphthalene* was obtained as an almost colourless oil, b. p. 140—144°/0·04 mm. (Found : C, 79·4; H, 8·9. $C_{17}H_{22}O_2$ requires C, 79·0; H, 8·5%), $\lambda_{max.}$ 2300 Å (ε 11,700).

6-Methoxy-2-3′-methoxybenzylidene-1-tetralone-A (*cis*?).—A solution of sodium (0·3 g.) in ethanol (10 ml.) was added to 6-methoxy-1-tetralone (5 g.) and *m*-methoxybenzaldehyde (6 g.) in boiling ethanol (35 ml.) with exclusion of air. A dark oil slowly separated. When poured into dilute acid the oil crystallised. When twice recrystallised from ethanol, *6-methoxy-2-3-methoxybenzylidene-1-tetralone*-A formed very pale yellow needles, m. p. 69° (Found: C, 78·0; H, 6·0. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·1%). This gave a 2 : 4-dinitrophenylhydrazone that was not obtained pure.

6-Methoxy-2-3′-methoxybenzylidene-1-tetralone-B (*trans*?) (V).—The preparation of the A-isomer was repeated, but the oil that separated was extracted with ether, the ether removed, and the residue distilled, giving a pale yellow oil. This was crystallised at −70° from ether, and on low-temperature crystallisation of the product *6-methoxy-2-3′-methoxybenzylidene-1-tetralone*-B was obtained as almost colourless needles, m. p. 57°. This m. p. could not be raised (mixed m. p. with A-isomer, 50°) (Found: C, 77·5; H, 6·2. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·1%). The 2 : *4-dinitrophenylhydrazone* was formed very slowly on the water-bath, and was obtained as dark red prisms, m. p. 197—198°, from chloroform (Found: C, 63·6; H, 4·5; N, 12·4. $C_{25}H_{22}O_6N_4$ requires C, 63·3; H, 4·6; N, 11·8%).

6-Methoxy-2-3′-methoxybenzyl-1-tetralone.—This was prepared by reduction of the two preceding isomers as in the preparation of the 2- and the 4-methoxybenzyl isomer. It was obtained as almost colourless prisms, m. p. 56° (Found : C, 76·8; H, 6·5. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·7%).

3 : *4-Dihydro-6-methoxy-1-(2-*p*-methoxyphenylethyl)naphthalene*.—6-Methoxy-1-tetralone (40 g.) in dry benzene (100 ml.) was added to a solution of 2-*p*-methoxyphenylethylmagnesium bromide (from magnesium, 5·65 g., and 2-*p*-methoxyphenylethyl bromide, 53 g.) in dry ether (300 ml.), and the resulting mixture boiled for 2 hr., then poured into excess of saturated aqueous ammonium chloride. Working up as above gave a viscous oil that was slowly distilled *in vacuo*. Dehydration occurred. The distillate solidified and was recrystallised from ethanol, yielding the *dihydronaphthalene*, plates, m. p. 84° (45 g.) (Found : C, 81·2; H, 7·3. $C_{20}H_{22}O_2$ requires C, 81·5; H, 7·5%).

1 : 2 : 3 : *4-Tetrahydro-6-methoxy-1-2′-*p*-methoxyphenylethylnaphthalene*.—The dihydro-compound (40 g.) in ethanol (140 ml.) was shaken with palladised strontium carbonate under hydrogen at atmospheric pressure and 45° until absorption of hydrogen ceased. The solution was freed from catalyst and alcohol, giving the *tetrahydronaphthalene*, b. p. 185°/0·04 mm. (38 g.) (Found : C, 81·4; H, 8·2. $C_{20}H_{24}O_2$ requires C, 81·1; H, 8·1%).

1 : 2 : 3 : 4 - *Tetrahydro-6-hydroxy-1-2′-*p*-hydroxyphenylethylnaphthalene*.—The preceding tetrahydronaphthalene (35 g.), glacial acetic acid (300 ml.), red phosphorus (2 g.), and concentrated hydriodic acid (200 ml.) were boiled together until evolution of methyl iodide ceased. The mixture was diluted with cold water (1 l.), and the precipitated oil extracted with ether. The ether extracts yielded a viscous oil that solidified on trituration with benzene. The solid, recrystallised from this solvent, gave the *phenol* as prisms, m. p. 95° (Found : C, 80·5; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%), readily soluble in alkali and giving a green colour with ferric chloride.

1 : 2 : 3 : 4-*Tetrahydro*-6-2′-*hydroxyethoxy*-2-2′-(p-2-*hydroxyethoxyphenyl*)*ethylnaphthalene*.—The foregoing phenol (20 g.) in excess of aqueous sodium hydroxide was heated on the water-bath for 4 hr. with ethylene chlorohydrin (20 g.), the mixture allowed to cool, and the liquid decanted from the orange-yellow glass. The glass was taken up in chloroform, dried, recovered, and distilled. The *ether* was a pale yellow oil, b. p. 250—255°/0·04 mm. (18 g.) (Found : C, 74·9; H, 8·2. $C_{22}H_{28}O_4$ requires C, 74·3; H, 7·9%).

1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*Octahydro*-6-*oxo*-1-(2-4′-*oxo*cyclo*hex*-2′-*enylethyl*)*naphthalene*.—The ether (17 g.) was reduced with sodium (20 g.), liquid ammonia (750 ml.), and ethanol (600 ml.) by the method described above. The product was isolated in ether and shaken therein for 4 hr. with 2N-hydrochloric acid to ensure hydrolysis of the enol ether. The extracts were then washed, dried, and evaporated, leaving a brown oil that was purified by distillation. 1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*Octahydro*-6-*oxo*-1-(2-4′-*oxo*cyclo*hex*-2′-*enylethyl*)*naphthalene* was obtained as an almost colourless oil, b. p. 185—190°/0·05 mm. (Found : C, 79·4; H, 9·6. $C_{18}H_{24}O_2$ requires C, 79·2; H, 8·9%).

1 : 2-*Di*-(4-*methoxy*cyclo*hexa*-1 : 4-*dienyl*)*ethanol* (XVI; R = OH, R′ = H).—A warm solution of *p*-anisoin (15 g.) in ethanol (75 ml.) and 2-ethoxyethanol (75 ml.) was added, followed by sodium (27 g.), to liquid ammonia (750 ml.) with vigorous stirring. When all the sodium had dissolved the mixture was poured into water (2 l.) and extracted twice with ether. The combined extracts were washed, dried, and evaporated, leaving a yellow oil that solidified and recrystallised from ethanol; 1 : 2-*di*-(4-*methoxy*cyclo*hexa*-1 : 4-*dienyl*)*ethanol* was obtained as prisms (11 g. crude, 5·5 g. pure), m. p. 112—113°, mixed m. p. with anisoin (m. p. 113°) 98—99° (Found : C, 73·1; H, 8·1. $C_{16}H_{22}O_3$ requires C, 73·3; H, 8·4%).

1 : 2-*Di*-(4-*methoxy*cyclo*hexa*-1 : 4-*dienyl*)*ethane* (XVI; R = R′ = H).—The mother-liquors from the recrystallisation of crude 1 : 2-di-(4-methoxy*cyclo*hexa-1 : 4-dienyl)ethanol were evaporated and the residual brown tar was boiled under reflux with ether and animal charcoal for 30 min., then filtered off. The ether was removed, leaving a yellow oil that was distilled, giving very pale yellow 1 : 2-*di*-(4-*methoxy*cyclo*hexa*-1 : 4-*dienyl*)*ethane*, b. p. 133—136°/0·025 mm. (Found : C, 78·3; H, 9·0. $C_{16}H_{22}O_2$ requires C, 78·0; H, 8·9%).

1 : 2-*Di*-(4-*methoxy*cyclo*hexa*-1 : 4-*dienyl*)*ethane*-1 : 2-*diol* (XVI; R = R′ = OH).—*p*-Anisil (15 g.) in ethanol (110 ml.) and 2-ethoxyethanol (110 ml.) was added to liquid ammonia (750 ml.) with vigorous stirring, followed by sodium (15 g.). More sodium and ethanol were added as the reduction proceeded until a total of 30 g. of sodium and 500 ml. of ethanol had been added. Working up as usual and recrystallisation from ethanol afforded 1 : 2-*di*-(4-*methoxy*cyclo*hexa*-1 : 4-*dienyl*)*ethane*-1 : 2-*diol*, pale yellow prisms, m. p. 122·5° (Found : C, 69·5; H, 7 6. $C_{16}H_{22}O_4$ requires C, 69·1; H, 7·9%).

4-(2-4′-*Oxo*cyclo*hex*-2′-*enylethylidene*)cyclo*hex*-2-*enone* (XVIII).—1 : 2-Di-(4-methoxy*cyclo*hexa-1 : 4-dienyl)ethanol (2·4 g.) in ether (40 ml.) was shaken with 2N-hydrochloric acid (25 ml.) for 16 hr. The ether layer was separated, the aqueous layer saturated with ammonium chloride and extracted once with ether, the combined ether solutions were dried, and the ether was removed. The residual yellow oily *ketone* was distilled three times *in vacuo*, the final distillate solidifying (Found : C, 77·2; H, 7·7. $C_{14}H_{16}O_2$ requires C, 77·7; H, 7·4%).

Glyoxylidenebis-4-cyclo*hex*-2-*enone* (XIX).—A solution of 1 : 2-di-(4-methoxy*cyclo*hexa-1 : 4-dienyl)ethane-1 : 2-diol (1·5 g.) in chloroform (10 ml.) was shaken with 2N-hydrochloric acid (20 ml.) for 5 hr. The chloroform layer was separated, washed, dried, and evaporated, leaving a dark brown oil that solidified, giving, on recrystallisation from chloroform, *glyoxylidenebis*-4-cyclo*hex*-2-*enone* as irregular yellow plates, m. p. 207° (Found : C, 78·9; H, 6·5. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%), $\lambda_{max.}$ 3100 Å (ε 27,000) indicating a highly conjugated system.

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