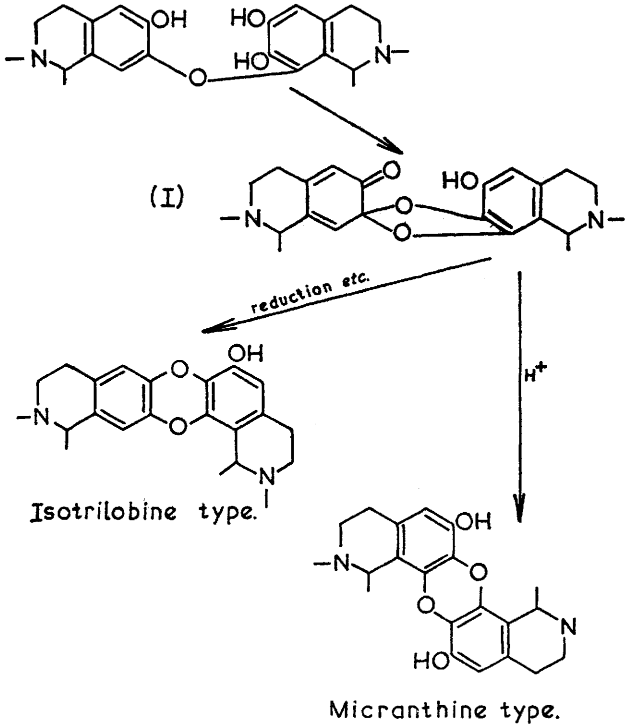
1,3-Benzodioxole-2-spirocyclohexadien-4′-one and Some of its Derivatives [1]

By **I. G. C. Coutts, D. J. Humphreys,** and **K. Schofield,*** Chemistry Department, University of Exeter

The synthesis of 2,4′-dihydroxydiphenyl ether, and of some of its homologues, and of some of the analogous dihydroxy-derivatives of naphthyl phenyl ethers is described. They were obtained by demethylating the corresponding methoxy-compounds. Oxidation of 2,4′-dihydroxydiphenyl ether gave a low yield of 1,3-benzodioxole-2-spirocyclohexadien-4′-one; five other examples of this type of conversion were observed. In particular, 4-(2-hydroxyphenoxy)-1-naphthol gave 1,3-benzodioxole-2-spiro-1′-naphthalen-4′-one in quantitative yield.

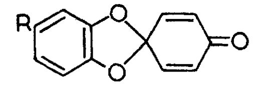
THE way in which the dibenzo-1,4-dioxin nucleus arises in such alkaloids as isotrilobine and micranthine is not known, nor is it easy to devise a simple scheme for its genesis by phenol oxidation followed by radical coupling. Such a scheme has been proposed by Barton and Cohen [2] but no evidence relating to it has been described. More recently Battersby [3] postulated a mechanism involving oxidation of a precursor to a phenoxy-radical or phenoxonium cation followed by radical or electrophilic substitution into a second isoquinoline nucleus; there is no evidence for the occurrence of such substitutions during phenol oxidation,[4] and Battersby [3] quotes an instance of the failure of such a substitution to occur in nature.

It occurred to us that a spirodienone of the type (I) might be involved in the genesis of the dibenzo-1,4-dioxin nucleus (Scheme). The spirodienone would be a kind of acetal not previously described and its ability to undergo the kind of rearrangement shown, in competition with other types of reaction, was therefore a matter of surmise. For this reason we undertook the synthesis of simple spirodienones of this type, and here report the preparation of six such compounds. A study of their reactions will be reported later; however we have not yet observed rearrangements of the desired type.



SCHEME

2,2′-Dihydroxydiphenyl ether was unaffected by potassium ferricyanide, by silver oxide, and by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The 2,4′-isomer and its 5-methyl derivative gave only insoluble precipitates with potassium ferricyanide. However, oxidation of 2,4′-dihydroxydiphenyl ether and its 4- and 5-methyl derivatives with silver oxide or DDQ gave the dienones (II; R = H or Me). The yields were low (1—2%), but it was later found that the use of manganese dioxide gave (II; R = H) in about 15% yield. *p*-Benzoquinone was a major product in all the oxidations with manganese dioxide.



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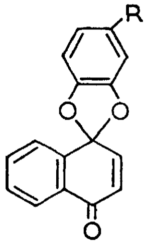

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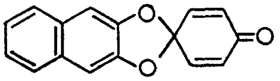

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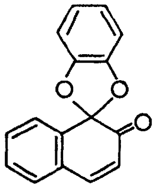

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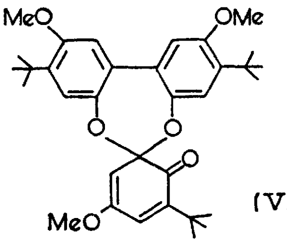

(VI)

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[1] Preliminary report, A. M. Choudbury, I. G. C. Coutts, A. K. Durbin, K. Schofield, and (in part) D. J. Humphreys, *Chem. Comm.*, 1968, 1341.

[2] D. H. R. Barton and T. Cohen, in 'Festschr. A. Stoll,' Birkhauser, Basel, 1957.

[3] A. R. Battersby, in 'Oxidative Coupling of Phenols,' Arnold, London, 1968.

[4] D. H. R. Barton, *Chem. in Britain*, 1967, **3**, 330.

4-(2-Hydroxyphenoxy)-1-naphthol was oxidised almost instantaneously by DDQ, giving a quantitative yield of (III; R = H). Surprisingly, the methyl compound (III; R = Me) was found in only 13% yield.

Less surprising was the failure of 3-(2-hydroxyphenoxy)-2-naphthol to give any trace of a carbonyl compound in reaction with DDQ. 3-(4-Hydroxyphenoxy)-2-naphthol likewise gave no dienone with DDQ but a large excess of manganese dioxide produced a very low yield of (IV). Our experience with 1-(2-hydroxyphenoxy)-2-naphthol was similar, but a better yield of a dienone resulted in this case. It was assigned the structure (V) rather than the obvious alternative on the basis of its n.m.r. spectrum.

The i.r. spectra of cyclohexa-2,5-dienones[5] commonly show bands in the regions 1640—1680, 1615—1650, and 1590—1620 cm.$^{-1}$. The compounds (III; R = H or Me) fitted into this pattern; however (II; R = H or Me) and (IV) showed an additional, weaker band at 1705 cm.$^{-1}$. Above 1500 cm.$^{-1}$ the spectrum of (V) contained only one strong band (at 1700 cm.$^{-1}$). The related compound (VI)[6] also shows carbonyl absorption at 1700 cm.$^{-1}$. The u.v. absorption spectra of the dienones show the features to be expected; in particular (V) absorbed at longer wavelengths than the 2,5-cyclohexadienones. The n.m.r. signal from the α-proton in cyclohexa-2,5-dienones generally appears at τ 3·6—4·0, and that from the α-proton in the 2,4-isomers at τ 4·0—4·2. In both cases the signal from a β-proton appears[5] at τ 2·85—3·25. The present compounds followed this behaviour, except that from (V) the signals were at τ 3·84 and 2·59.

Starting Materials.—The phenolic diaryl ethers from which the dienones were obtained were all prepared by demethylating the corresponding dimethyl ethers. 2-Methoxy-1-naphthol has been prepared previously[7,8] but in unsatisfactory yield. By oxidising 2-methoxy-1-naphthylmagnesium bromide with oxygen[8] we obtained the phenol in only 1% yield. 6-Methoxy-2-naphthol has been prepared[9] by oxidising the corresponding boronic ester. Applied to the present case this method gave only 4,4′-dihydroxy-3,3′-dimethoxy-1,1′-binaphthyl but a minor modification, whereby the ester was hydrolysed to the boronic acid, which was then oxidised, gave 2-methoxy-1-naphthol in 50% yield.

All the naphthyl phenyl ethers were prepared by use of the conditions described by Bacon and Hill[10] for other cases. In every case substitutive reduction of the aryl halide was a competing reaction, and where 1-iodo-2-methoxynaphthalene was used, this was the major reaction.

The dimethoxy-compounds were smoothly demethylated with pyridine hydrochloride. The temperature of reaction was critical: if it were too high decomposition occurred, if too low the reaction was incomplete.

Attempts to prepare certain dinaphthyl ethers were almost wholly unsuccessful (see Experimental section).

EXPERIMENTAL

Light petroleum used had b.p. 60—80° unless otherwise stated.

2,4′-Dimethoxydiphenyl Ether.—*p*-Bromoanisole (93·5 g.), guaiacol (62 g.), anhydrous potassium carbonate (50 g.), pyridine (10 ml.), and precipitated copper (10 g.) were heated together under reflux at 170° for 5 hr.; further copper (10 g.) and pyridine (10 ml.) were added after 2 hr. The cooled mixture was treated with dilute hydrochloric acid and extracted with ether. The extract was washed with sodium hydroxide solution, dried, and concentrated. The residue was diluted with light petroleum and kept overnight at −10° to give the product (47 g.), m.p. 72—74° (lit.,[11] 77°).

2,4′-Dihydroxydiphenyl Ether.—The dimethyl compound (35 g.), benzene (100 ml.), and powdered aluminium chloride (100 g.) were heated at 120° for 1 hr. The cooled mixture was treated with ice and dilute hydrochloric acid. The precipitate was dissolved in alkali and reprecipitated by acidification. *2,4′-Dihydroxydiphenyl ether* gave crystals (23 g.), m.p. 164—165° (from chloroform–light petroleum) (Found: C, 71·6; H, 5·3. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

2,4′-Dimethoxy-4-methyldiphenyl Ether.—Prepared from creosol as above the *ether* (35%) was purified by distillation (b.p. 204—205°) and gave prisms, m.p. 55—56° (from light petroleum) (Found: C, 73·5; H, 6·2. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·5%).

2,4′-Dihydroxy-4-methyldiphenyl Ether.—Prepared as described above (50%) this *ether* gave crystals, m.p. 136—137° (from chloroform–carbon tetrachloride) (Found: C, 71·8; H, 5·6. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

2,4′-Dimethoxy-5-methyldiphenyl Ether.—Prepared from isocreosol (33%) the *ether* was an oil, b.p. 206—207°/15 mm. (Found: C, 73·2; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·5%).

2,4′-Dihydroxy-5-methyldiphenyl Ether.—Prepared by demethylation of the above compound (55%), this *ether* gave crystals, m.p. 140—141° (from chloroform–carbon tetrachloride) (Found: C, 71·8; H, 5·5. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

2-Methoxy-1-naphthol.—(*a*) A Grignard solution prepared from 1-bromo-2-methoxynaphthalene[12] (59·3 g.) in tetrahydrofuran (200 ml.) was added during 10 min. to trimethyl borate (37·5 ml.) in dry ether (130 ml.) stirred at −70° under nitrogen. The paste which formed immediately was stirred for 30 min. and kept at room temperature under nitrogen overnight. The mixture was acidified with dilute hydrochloric acid, the organic layer was separated, and the aqueous layer was extracted several times with ether. Removal of the solvent from the combined solutions gave a pale yellow solid (86 g.) which was stored under nitrogen at −10°.

This product (39 g.) was dissolved in N-sodium hydroxide (750 ml.), the solution was filtered, and 15% hydrogen

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[5] A. J. Waring, in *Adv. Alicyclic Chem.*, 1966, **1**, 131.

[6] F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc.*, 1965, 3660.

[7] H. S. Chang and J. T. Edward, *Canad. J. Chem.*, 1963, **41**, 1233.

[8] S. N. Chakravarti and V. Pasupati, *J. Chem. Soc.*, 1937, 1859.

[9] R. L. Kidwell and S. D. Darling, *Tetrahedron Letters*, 1966, 531.

[10] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1964, 1108.

[11] P. A. Sartoretto and F. J. Sowa, *J. Amer. Chem. Soc.*, 1937, **59**, 603.

[12] N. P. Buu-Hoï, *Annalen*, 1964, **556**, 1.

peroxide (120 ml.) was added. After 5 min. the mixture was acidified and extracted with ether. Removal of the ether after drying gave a tarry oil which was extracted with boiling light petroleum (b.p. 40—60°). Removal of the solvent and recrystallisation from the same solvent gave 2-methoxy-1-naphthol (9·8 g.), m.p. 54—55°.

The importance of filtering the alkaline solution before carrying out oxidation was not at first appreciated, and the material from which a specimen of 1-(4-hydroxyphenoxy)-2-naphthol was obtained (see later) contained about 20% of 2-methoxynaphthalene formed by decomposition of the boronic ester.

(*b*) A Grignard solution was prepared from 1-bromo-2-methoxynaphthalene (118·5 g.) as in (*a*) and run into trimethyl borate (75 ml.) in dry ether (250 ml.), stirred under nitrogen at −70°. The paste which formed immediately was allowed to reach room temperature overnight.

To the ice-cold solution of the boronic ester was added a cold solution of ammonium chloride (100 g.) in 15% hydrogen peroxide (1500 ml.). The temperature rose to 35° and the mixture was stirred for 1 hr. Volatile solvents were removed and the precipitate was collected, washed with water, and dissolved as far as possible in 2N-sodium hydroxide. An insoluble residue remained. The alkaline solution was acidified, and the precipitate was washed with water and gave greenish plates of 4,4′-dihydroxy-3,3′-dimethoxy-1,1′-binaphthyl, m.p. 275° (from ethanol) (Found: C, 76·0; H, 5·3; MeO, 16·6. Calc. for $C_{22}H_{18}O_4$: C, 76·3; H, 5·2; MeO, 17·9%) [lit.,[7] m.p. 260—261°; lit.,[13] 288° (decomp.)], $\nu_{max.}$ (KBr) 3400 cm.$^{-1}$, τ [$(CD_3)_2SO$] 0·71 (2H, s, exchangeable 2 × OH), 1·77 and 1·90 (each 1H, s), 2·45—3·00 (8H, m), and 6·11 (6H s, 2 × OMe). The compound was acetylated with acetic anhydride–sodium acetate. The product gave the *diacetate*, m.p. 244—246° (from ethanol) (Found: C, 71·8; H, 4·8; Ac, 18·5. $C_{26}H_{22}O_6$ requires C, 72·5; H, 5·1; Ac, 20·0%).

2-*Methoxy*-1-(2-*methoxyphenoxy*)*naphthalene*.—(*a*) 2-Methoxy-1-naphthol (8·7 g.), *o*-bromoanisole (9·35 g.), copper(I) oxide (3·6 g.), and collidine (200 ml.) were stirred and heated together at 170° under nitrogen for 48 hr. The collidine was removed *in vacuo* and the residue was repeatedly extracted with boiling light petroleum. A solution of the petroleum-soluble material in ether was washed successively with dilute hydrochloric acid, sodium hydroxide solution, and water, and dried. Ether, anisole, and *o*-bromoanisole were distilled off (the second two at an oil pump). Recrystallisation from light petroleum (charcoal) gave crystals (40 mg.), m.p. 90—94°, identical with those described later.

(*b*) 1-Iodo-2-methoxynaphthalene (28·4 g.), guaiacol (12·4 g.), copper(I) oxide (7·2 g.), and collidine (400 ml.) were stirred and heated together at 170° under nitrogen for 72 hr. The collidine was removed *in vacuo*. The residue in chloroform was washed with dilute hydrochloric acid, sodium hydroxide solution, and water, and dried. Removal of the solvent left a solid (14·4 g.). This was chromatographed on silica gel (110 × 2 cm.) in light petroleum–benzene (1 : 1). The first fraction (10·6 g.) was a mixture of 2-methoxynaphthalene with a trace of the 1-iodo-compound. Further elution with benzene gave a pale yellow oil which on treatment with ethanol gave the *dimethoxy-compound* (2·55 g., m.p. 97—98°), m.p. 98—99° (from ethanol) (Found: C, 76·8; H, 5·9. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·75%), τ ($CDCl_3$) 2·0—3·8 (10H, m) and 6·00 and 6·16 (each 3H, s, OMe).

1-(2-*Hydroxyphenoxy*)-2-*naphthol*.—The dimethyl ether (2 g.) and pyridine hydrochloride (21 g.) were heated together under nitrogen at 180—190° for 2·5 hr. with stirring. The cooled mixture was diluted with water and extracted with ether. The ether solution was extracted with sodium hydroxide solution, and the extract was acidified with hydrochloric acid and re-extracted with ether. Removal of the ether and crystallisation of the residue from chloroform gave the *diphenol* (1·8 g.), m.p. 159—161° (Found: C, 75·7; H, 4·7. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%), τ [$(CD_3)_2SO$] 0·4br (2 × OH) and 2·0—3·9 (10H m).

1-(4-*Hydroxyphenoxy*)-2-*naphthol*.—As already described the preparation of this compound, carried out exactly as for its isomer, used a specimen of 2-methoxy-1-naphthol contaminated with 2-methoxynaphthalene. After demethylation, 2-naphthol and the product were separated by chromatography on neutral alumina (chloroform and chloroform–methanol). 1-(4-*Hydroxyphenoxy*)-2-*naphthol* formed colourless needles, m.p. 203—205° (from chloroform) (Found: C, 75·6; H, 4·75. $C_{16}H_{12}O_3$ requires C, 76·1; H, 4·8%).

2-*Methoxy*-3-(2-*methoxyphenoxy*)*naphthalene*.— 3-Methoxy-2-naphthol (4 g.), *o*-bromoanisole (4·3 g.), copper(I) oxide (1·8 g.), and collidine (100 ml.) were heated together under nitrogen at 170° for 72 hr. Work-up as before gave, after removal of anisole and a trace of *o*-bromoanisole, and crystallisation from chloroform–light petroleum, 2-*methoxy*-3-(2-*methoxyphenoxy*)*naphthalene* (1·1 g., m.p. 86—87°), m.p. 88—89° [from light petroleum (b.p. 40—60°)] (Found: C, 76·9; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·75%), τ ($CDCl_3$) 2·1—3·2 (10H, m) and 6·04 and 6·22 (each 3H, s, OMe).

3-(2-*Hydroxyphenoxy*)-2-*naphthol*.—Demethylated for 3 hr. as already described the dimethyl ether (670 mg.) gave the product (600 mg.). The *diphenol* formed needles, m.p. 129—130° (Found: C, 76·7; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%), from chloroform–light petroleum.

2-*Methoxy*-3-(4-*methoxyphenoxy*)*naphthalene*.— By the method already described 3-methoxy-2-naphthol (14 g.) and *p*-bromoanisole (15 g.) gave a product which on crystallisation from light petroleum (charcoal) gave the *ether* (8·9 g.), m.p. 103—105° (Found: C, 77·1; H, 5·9. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·75%), τ ($CDCl_3$) 2·1—3·2 (10H, m), and 6·02 and 6·21 (each 3H, s, OMe).

3-(4-*Hydroxyphenoxy*)-2-*naphthol*.—The dimethyl ether (8 g.) was demethylated like its isomer. The crude product (7 g.) was freed from traces of impurity by passage over neutral alumina (50 × 2 cm.) in chloroform. The *phenol* crystallised as needles, m.p. 164—166° (from chloroform) (Found: C, 75·8; H, 4·75. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%), τ [$(CD_3)_2SO$] 0·25 and 0·60 (partly superimposed, broad, each 1H, OH) and 2·4—3·4 (10H, m).

1-*Methoxy*-4-(2-*methoxyphenoxy*)*naphthalene*.— 1-Bromo-4-methoxynaphthalene prepared by brominating 1-methoxynaphthalene,[14] was a pale yellow oil, b.p. 112—116°/0·04 mm. (lit.,[14] 148—150°/0·1 mm.). The following experiment showed it to contain some 1,3-dibromo-4-methoxynaphthalene.

(*a*) 1-Bromo-4-methoxynaphthalene (29·6 g.), guaiacol (15·5 g.), copper(I) oxide (9 g.), and collidine (500 ml.) were heated with stirring at 170° for 90 hr. under nitrogen. The

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[13] F. R. Hewgill and B. S. Middleton, *J. Chem. Soc.* (*B*), 1967, 2316.

[14] J. Szmuszkovicz and E. J. Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 566.

collidine was removed *in vacuo* and the residue was repeatedly extracted with light petroleum. The soluble material was washed in ether with dilute hydrochloric acid, sodium hydroxide solution, and water. Removal of the ether after drying, followed by distillation, gave fractions b.p. 90—150°/9·1 mm. and 150—170°/0·1 mm., and a residue. T.l.c. (Eastman Chromagram Sheet, n-hexane) showed the first fraction to consist of 1-methoxynaphthalene and 1-bromo-4-methoxynaphthalene (R_F 0·78 and 0·77, respectively). Similarly (benzene–petroleum, 1 : 1) the second fraction was shown to contain the bromo-compound (R_F 0·75) and a new component (R_F 0·58). The residue showed two spots R_F 0·58 and 0·35, and gave on distillation a syrup, b.p. 174—182°/0·1 mm. (R_F 0·58) and a second residue. The second residue was chromatographed on a column of silica gel (110 × 2 cm.) in benzene–light petroleum (1 : 1). Fractions (250 ml.) were examined by t.l.c. (benzene–light petroleum, 1 : 1) as follows: fraction 1 (R_F 0·75 and 0·58), fractions 2—11 (R_F 0·58), fractions 12—14 (R_F 0·58 and 0·35), fraction 15 onwards (R_F 0·35). Distillation of fractions 2—11 gave a syrup, b.p. 174—175°/0·2 mm., which was combined with the syrup already mentioned. The combined fractions were cleaned by passage in chloroform over neutral alumina. The resulting oil gave crystals of 1-*methoxy*-4-(2-*methoxyphenoxy*)*naphthalene* (11·9 g.), m.p. 79—80° (from ethanol) (Found: C, 76·95; H, 5·6. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%), τ (CDCl$_3$) 1·6—1·95 (2H, m), 2·35—2·65 (2H, m), 2·90—3·30 (6H, m), and 6·06 and 6·12 (each 3H, s, OMe).

The oil from fraction 15 onwards (1·2 g.) gave from n-butanol crystals of 1-*methoxy*-2,4-*bis*-(2-*methoxyphenoxy*)-*naphthalene*, m.p. 101—102° (Found: C, 74·5; H, 5·6. $C_{22}H_{22}O_5$ requires C, 74·6; H, 5·5%), τ (CDCl$_3$) 1·6—1·9 (2H, m), 2·3—2·7 (2H, m), 2·95—3·30 (8H, m), 3·45 (1H, s), and 5·99, 6·18, and 6·21 (each 3H, s, OMe).

In further preparations 1-bromo-4-methoxynaphthalene (29·6 g.), guaiacol (46·6 g.), collidine (500 ml.), and copper(I) oxide (27 g.) were heated together under reflux for 96 hr. The neutral, light petroleum-soluble product was chromatographed on a column of silica gel. Elution with light petroleum gave 1-bromo-4-methoxynaphthalene and a little 1-methoxynaphthalene. Elution with light petroleum–benzene (2 : 1) then gave the product as a thick oil. Trituration with ethanol removed a yellow impurity and left the crystalline product (18·2 g.), m.p. 79—80°.

(*b*) Copper(II) oxide [15] (12·5 g.) was added to a boiling solution of 1-bromo-4-methoxynaphthalene (29·6 g.) and guaiacol (46·6 g.) in pyridine (80 ml.) and the mixture was heated at 150° under nitrogen for 24 hr. Pyridine was removed *in vacuo* and the residue was poured into ether. The mixture was filtered and the filtrate was washed with sodium hydroxide solution, dilute hydrochloric acid, and water, and dried. Removal of the solvent left neutral material (35·2 g.) which was chromatographed on silica gel as already described, giving 1-methoxy-4-(2-methoxyphenoxy)naphthalene (17·4 g.), m.p. 79—80°.

4-(2-*Hydroxyphenoxy*)-1-*naphthol*.—The dimethyl ether (10 g.) and pyridine hydrochloride [from pyridine (30 ml.)] were stirred together under nitrogen at 180—190° for 3 hr. Work-up in the usual way and chromatography on alumina (pH 6; 40 × 2 cm.) in chloroform gave 4-(2-*hydroxyphenoxy*)-1-*naphthol* (6·9 g., m.p. 151°), m.p. 151—152° (from chloroform) (Found: C, 75·6; H, 4·75. $C_{16}H_{12}O_3$ requires C, 76·1; H, 4·8%), τ [(CD$_3$)$_2$SO] 0·10 and 0·57 (each 1H, sharp s, OH), 1·7—2·1 (2H, m), 2·4—2·7 (2H, m), and 3·0—3·4 (6H, m). Solutions of the phenol in chloroform became red.

From a demethylation carried out at 170—180°, as well as the diphenol a small amount of a monomethyl ether, m.p. 118—120°, was isolated, τ (CDCl$_3$) 1·55—2·05 (2H, m), 2·35—2·65 (2H, m), 2·85—3·45 (6H, m), 4·11br (1H, OH), and 6·05 (3H, s, OMe), *m/e* 266, 251, and 158.

From some preparations at the higher temperature a second phenol was obtained along with the main product, from which it was separated by use of its lower solubility in chloroform. It crystallised from chloroform as colourless needles, m.p. 176—178° (Found: C, 82·55; H, 4·5. $C_{16}H_{10}O_2$ requires C, 82·0; H, 4·3%), $\nu_{max.}$ (KBr) 3310 cm.$^{-1}$, τ [(CD$_3$)$_2$SO] −0·33 (1H, s), and 1·5—3·1 (9H, m), *m/e* 234, $\lambda_{max.}$ (EtOH) 215 (ε 16,700), 237 (35,800), 257 (30,900), 264 (45,100), 285 (10,1000), 288 (10,000), 296 (11,200), 310 (5300), 317sh (3400), 325 (4100), 332 (2200), and 340 (5200) nm.

1-*Methoxy*-4-(2-*methoxy*-4-*methylphenoxy*)*naphthalene*.—1-Bromo-4-methoxynaphthalene (23·7 g.), creosol (13·8 g.), copper(I) oxide (7·7 g.), and collidine (400 ml.) were stirred and heated at 170° under nitrogen for 72 hr. The mixture was worked up as before and the crude product was distilled to remove 1-bromo-4-methoxynaphthalene, b.p. 127—140°/0·4 mm. The residue was chromatographed on silica gel (110 × 2 cm.). Elution with light petroleum gave more of the starting bromide; elution with light petroleum–benzene (1 : 1) gave a yellow oil from which a solid (6 g.) was obtained by trituration with ethanol. Recrystallisation from ethanol gave the *dimethyl ether*, m.p. 105—107° (Found: C, 77·6; H, 6·1. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%), τ (CDCl$_3$) 1·55—1·90 (2H, m), 2·30—2·60 (2H, m), 3·05—3·45 (5H, m), 6·04 and 6·12 (each 3H, s, OMe), and 7·67 (3H, s, Me).

4-(2-*Hydroxy*-4-*methylphenoxy*)-1-*naphthol*.—The above compound (1·48 g.) was demethylated as already described, at 170—180° for 3 hr. Work-up as before gave as the acidic fraction a red oil which was dissolved in chloroform and left to crystallise. A solid (506 mg.) separated, which gave the *diphenol*, m.p. 146—147° (from chloroform) (Found: C, 76·3; H, 5·3. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

Bis-(2-*methoxy*-1-*naphthyl*) *Ether*.—(*a*) 1-Bromo-2-methoxynaphthalene (9·5 g.), 2-methoxy-1-naphthol (7 g.), copper(I) oxide (3 g.), and collidine (200 ml.) were heated together at 170° under nitrogen for 48 hr. The mixture was poured into 6N-hydrochloric acid (500 ml.) and extracted with benzene. The benzene solution was washed with dilute hydrochloric acid, sodium hydroxide solution, and water, some tar being deposited. After drying, the benzene was removed and the oil (which slowly crystallised) was chromatographed on silica gel (50 × 3 cm.). Elution with light petroleum–benzene (3 : 1) gave a mixture (6·2 g.) of 2-methoxynaphthalene and 1-bromo-2-methoxynaphthalene. Further elution with light petroleum–benzene (1 : 1) gave a solid (310 mg.) which yielded a mixture of needles and more dense crystals from light petroleum. These were separated manually; crystallisation of the denser substance gave *bis*-(2-*methoxy*-1-*naphthyl*) *ether*, m.p. 92—93° (Found: C, 79·9; H, 5·5. $C_{22}H_{18}O_3$ requires C, 79·9; H, 5·5%), τ (CDCl$_3$) 1·6—3·0 (12H, m), and 6·61 (6H, s 2 × OMe), *m/e* 330 (M^+). The second product was not identified.

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[15] M. Tomita, K. Fujitani, and Y. Aoyagi, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 1341.

(*b*) 1-Iodo-2-methoxynaphthalene (14·2 g.), 2-methoxy-1-naphthol (8·7 g.), copper(I) oxide (3·6 g.), and collidine (200 ml.) were stirred and heated at 170° under nitrogen for 72 hr. The mixture was worked up as before up to the point where the washed and dried benzene extract was evaporated. The residue was extracted with boiling light petroleum giving as the soluble material a solid (8·1 g.) which was chromatographed on silica gel (50 × 3 cm.). Elution with petroleum–benzene (3 : 1) gave 2-methoxynaphthalene (6·4 g.). Further elution with benzene gave the product (125 mg.), m.p. 91—92°.

1,3-*Benzodioxole*-2-*spirocyclohexadien*-4′-*one*.—(*a*) To a boiling solution of 2,4′-dihydroxydiphenyl ether (15·1 g.) in benzene (1·5 l.) was added quickly a hot solution of DDQ (17·1 g.) in benzene (500 ml.). A dark colour developed immediately and a precipitate started to appear. The mixture was boiled under nitrogen for 2 hr., cooled, and filtered. The filtrate was concentrated under reduced pressure to 50 ml. and again filtered. The filtrate was passed down a column of silica gel (75 g. of Mallinckrodt ' Silicar ' CC-4) packed in benzene, and the column was eluted with this solvent. Evaporation of the first clear-cut yellow fraction gave the *dienone* (240 mg.) as yellow prisms, m.p. 144—145° (Found: C, 71·8; H, 4·2. $C_{12}H_8O_3$ requires C, 72·0; H, 4·0%), $\nu_{\text{max.}}$ (KBr) 1675 and 1640 cm.$^{-1}$, $\lambda_{\text{max.}}$ (cyclohexane) 217 (ε 19,950), 235sh (5370), 270sh (3980), 274 (4570), 279 (4677), and 285 (3467) nm., τ ($CDCl_3$) 3·1 and 3·7 (2H, *J* 10 Hz) and 3·1 (4H, s).

The benzene-insoluble material (26·7 g.) formed in the oxidation was boiled with methanol (700 ml.). The undissolved buff powder (3·9 g.) was insoluble in common solvents and in alkali. Its i.r. spectrum showed no hydroxy-absorption, only a very weak cyanide band, and very strong absorption at 1480 and 1200 cm.$^{-1}$. Evaporation of the methanolic solution and boiling the residue with chloroform (350 ml.) left dichlorodicyanohydroquinone (14·1 g.) undissolved. The chloroform contained two unidentified components [R_F 0·3 and 0·7 (t.l.c. on silica gel with 10% methanol–chloroform)].

(*b*) To a solution of the phenol (25 g.) in hot benzene (1·5 l.) was added manganese dioxide [16] (100 g.), and the vigorously stirred mixture was maintained at 70° for 15 hr. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure and put on a silica gel column (100 g., in benzene). Elution with benzene gave the dienone (3·2—4·3 g.), m.p. 143—144°. Further elution with 3% methanol–benzene gave *p*-benzoquinone, m.p. 114—115°, identified by comparison with authentic material.

5-*Methyl*-1,3-*benzodioxole*-2-*spiro*-*cyclohexadien*-4′-*one*.—(*a*) Oxidation of either 2,4′-dihydroxy-4- or -5-methyldiphenyl ether with DDQ as before gave the *dienone*, which separated from light petroleum as yellow needles (1·5—2%), m.p. 88—89° (Found: C, 73·1; H, 4·6. $C_{13}H_{16}O_3$ requires C, 72·9; H, 4·7%), $\nu_{\text{max.}}$ (KBr) 1680 cm.$^{-1}$, τ (CCl_4) 3·22 and 3·82 (4H, *J* 10 Hz), 3·38 (3H, s), and 7·73 (3H, s).

(*b*) The use of manganese dioxide with either phenol gave the dienone in 8·5% yield. Examination of the crude oxidation mixture by t.l.c. showed the ratio of benzoquinone to dienone to be about 1 : 1 from the 4-methyl compound, and about 3 : 1 from the 5-methyl compound.

1,3-*Benzodioxole*-2-*spiro*-1′-*naphthalen*-4′-*one*.—4-(2-Hydroxyphenoxy)-1-naphthol (100 mg.) in benzene (20 ml.) was treated with DDQ (90 mg.) in benzene (10 ml.) and the mixture was stirred for 30 min. at room temperature. The precipitate of dichlorodicyanohydroquinone was removed, and the filtrate was evaporated. The residue in benzene was passed over silica gel (30 × 1 cm.) to give a colourless solid (100 mg., m.p. 100—101°), which gave needles of the *dienone*, m.p. 104·5—105° (from light petroleum) (Found: C, 76·8; H, 4·1. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%), $\nu_{\text{max.}}$ (KBr) 1675, 1635, and 1600 cm.$^{-1}$, τ ($CDCl_3$) 1·8—2·0 (1H, m), 2·2—2·55 (3H, m), 3·10 (4H, s), and 3·04 and 3·61 (2H, AB pair, *J* 10 Hz), $\lambda_{\text{max.}}$ (cyclohexane) 265 (ε 6800), 274 (7500), 278 (7700), 284 (7550), 290 (6100), and 310sh (900) nm.

5-*Methyl*-1,3-*benzodioxole*-2-*spiro*-1′-*naphthalen*-4′-*one*.—To a warm (50°) solution of the corresponding diphenol (409 mg.) in benzene (25 ml.) was added a warm solution of DDQ (350 mg.) in benzene (15 ml.). The mixture was stirred for 30 min. at room temperature and filtered. The concentrated filtrate was chromatographed (benzene) on neutral alumina (40 × 1 cm.) giving the product as a crystalline solid (52 mg.). The *dienone* gave pale yellow needles, m.p. 109—110° (from light petroleum) (Found: C, 77·2; H, 5·3. $C_{17}H_{12}O_3$ requires C, 77·3; H, 4·6%), $\nu_{\text{max.}}$ (KBr) 1675, 1635, and 1600 cm.$^{-1}$, τ ($CDCl_3$) 1·70—1·95 (1H, m), 2·1—2·35 (3H, m), 3·21 (3H, s), 2·95 and 3·53 (2H, AB pair, *J* 10·5 Hz), and 7·67 (3H, s, Me), $\lambda_{\text{max.}}$ (cyclohexane) 265 (ε 7740), 279 (8300), 284 (8400), 290 (7800), and 296 (6050) nm.

1,3-*Naphtho*[2,3]*dioxole*-2-*spirocyclohexadien*-4′-*one*.—The appropriate phenol (1·5 g.), benzene (750 ml.), and active manganese dioxide (7·5 g.) were stirred at room temperature for 4·5 hr. The mixture was filtered and the solid was extracted with boiling benzene. The combined benzene solutions were concentrated *in vacuo*. Chromatography (benzene) of the residue on neutral alumina (40 × 1 cm.) gave the product (20 mg., m.p. 157—158°) as the first fraction. The *dienone* gave colourless needles, m.p. 162—163° (from light petroleum) (Found: C, 76·85; H, 4·0. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%), $\nu_{\text{max.}}$ (KBr) 1705, 1690, 1650, and 1620 cm.$^{-1}$, τ ($CDCl_3$) 2·15—2·85 (6H, m) and 3·10 and 3·67 (4H, AB pair, *J* 10 Hz), $\lambda_{\text{max.}}$ (cyclohexane) 256 (ε 7400), 266 (7600), 276 (7000), 287 (4900), 299 (2300), 305 (2800), 312 (4000), 318 (3800), and 326 (5000) nm.

1,3-*Benzodioxole*-2-*spiro*-1′-*naphthalen*-2′-*one*.— The diphenol (484 g.), benzene (250 ml.), and active manganese dioxide (2·5 g.) were stirred together for 24 hr. at room temperature. The solution, after centrifugation, was evaporated to give a gum (490 mg.). This material was chromatographed on neutral alumina (30 × 1 cm.). Elution with chloroform gave a gum (72 mg.) which was subjected to thick-layer chromatography on silica gel G in benzene. Four bands were obtained, R_F 0·57, 0·38—0·49, 0·17, and 0·04. The first was due to a pale yellow solid (3 mg.), and the second to a bright yellow oil (53 mg.) which slowly crystallised. The latter gave yellow needles of the *dienone*, m.p. 107·5—108° [from light petroleum (b.p. 40—60°)] (Found: C, 76·8; H, 4·1. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%), $\nu_{\text{max.}}$ (KBr) 1700 cm.$^{-1}$, τ ($CDCl_3$) 2·1—2·8 (4H, m), 3·12 (4H, s), and 2·59 and 3·84 (2H, AB pair, *J* 10 Hz), $\lambda_{\text{max.}}$ (cyclohexane) 275sh (ε 5300), 280 (6000), 285 (6500), 291 (6200), 322 (7500), and 350sh (1900) nm.

[9/598 *Received, April* 10*th*, 1969]

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[16] B. Franck and A. Blaschke, *Annalen*, 1963, **668**, 145.