

## Spirodienones. Part 2.<sup>1</sup> The Synthesis of Some Heterocyclic Spirodienones by Phenolic Coupling

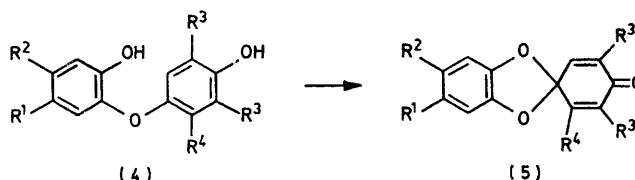
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The oxidation with active manganese dioxide of a series of 2,4'-dihydroxydiphenyl ethers to the corresponding *p*-benzoquinone monoacetals (1,3-benzodioxole-2-spirocyclohexadien-4'-ones) is described; among the dienones prepared were monoacetals of nitro-*p*-benzoquinone and of *p*-fluoranil. Attempted ether formation with 2,6-di-*t*-butyl-4-bromophenol and either 2- or 3-methoxyphenol failed, small quantities of unsymmetric biphenyls being formed in a novel arylation reaction. A spirobenzoxazole can be prepared by oxidation of a 2,4'-dihydroxydiphenylamine. Substituent effects in the hydrolysis of derived spirodienols have been observed.

SINCE the monoacetals of *p*-benzoquinones (1) are potentially attractive intermediates in synthesis, there has been much recent interest in their preparation. They are usually obtained by the selective hydrolysis of quinone bisacetals (2) (available from anodic oxidation of 1,4-dialkoxy-<sup>2</sup> or monomethoxy-<sup>3</sup> benzenes) or by the oxidation<sup>4</sup> of *p*-alkoxyphenols with thallium(III) nitrate or with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in alcoholic solvents. Monoacetals have also been prepared by photochemical cyclisation<sup>5</sup> of substituted phenoxyethanols.

There has, however, been little work on compounds (1) in which a quinone carbonyl is acetalised by phenol rather than alcohol functions. Hewgill and his co-workers have described<sup>6</sup> the isolation of dioxepins such as (3) from the oxidative trimerisation of substituted

dienones (5) was studied.<sup>9</sup> It was established that treatment of ethers (6) and (7) with active manganese dioxide gave the dienones (17) and (18) in 10–15% yield, while an acetal of 1,4-naphthaquinone is formed quantitatively by the oxidation of 4-(2-hydroxyphenoxy)-1-naphthol with DDQ.



(4)

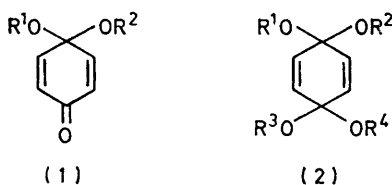
(5)

(6)  $R^1 = R^2 = R^3 = R^4 = H$ 

(17) (10–15%)

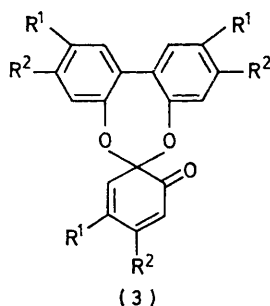
(7)  $R^1 = Me; R^2 = R^3 = R^4 = H$ 

(18) (10%)

(8)  $R^2 = Me; R^1 = R^3 = R^4 = H$ (9)  $R^1 = NO_2; R^2 = R^3 = R^4 = H$ (10)  $R^2 = NO_2; R^1 = R^3 = R^4 = H$  (19) (39%)(11)  $R^1 = CO_2Me; R^2 = R^3 = R^4 = H$  (20) (18%)(12)  $R^2 = CO_2Me; R^1 = R^3 = R^4 = H$ (13)  $R^1 = R^2 = R^3 = H; R^4 = NO_2$  (21) (15%)(14)  $R^1 = R^2 = R^3 = H; R^4 = CO_2Me$  (22) (35%)(15)  $R^1 = R^2 = R^4 = H; R^3 = Me$  (23) (10%)(16)  $R^1 = R^2 = R^4 = H; R^3 = Bu^t$ 

(1)

(2)



(3)

monophenols, while a dioxepin is also formed by treatment of 2,4-diphenylphenol with alkaline ferricyanide.<sup>7</sup> Halogenated monoacetals have been prepared<sup>8</sup> from tetrahalogeno-*o*-quinones.

### RESULTS AND DISCUSSION

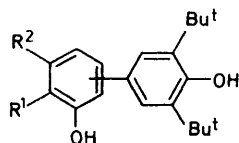
In a preliminary attempt to devise an efficient synthesis of phenol-derived monoacetals, the oxidation of 2,4'-dihydroxydiphenyl ethers (4) to the corresponding spiro-

To explore the versatility of this method of obtaining quinone acetals, the substituted dihydroxydiphenyl ethers (10)–(15) have been synthesised by standard methods (see Experimental section) and oxidised with active manganese dioxide to the dienones (19)–(23). By analogy with other intramolecular phenol coupling reactions,<sup>10</sup> it seemed possible that the oxidation of compounds (4) might proceed by synchronous oxidation of both hydroxy-groups to a diradical which would then form the dienones (5). Thus substituents which prolong the lifetime of one phenoxyl radical, or which minimise intermolecular reaction, should lead to an increased yield of internally coupled product. Some evidence of this was obtained on oxidation of ethers (10), (11), and (14) (see Table). The comparatively low yield of nitro-dienone (21) from (13) is due to the limited stability of the product which is, however, greater than that of nitro-*p*-benzoquinone;<sup>11</sup> no acetals of nitroquinones have previously been reported.

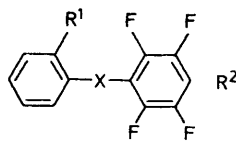
The disubstituted phenol (15) did not form dienone

(23) in high yield perhaps because of hydrogen-atom abstraction from the methyl groups. However, attempts to synthesise the more hindered phenolic ether (16) led to unexpected difficulties. Reaction of 2-methoxyphenol with 2,6-di-*t*-butyl-4-bromophenol in the presence of copper, pyridine, and potassium carbonate, gave 3,3',5,5'-tetra-*t*-butyldiphenyl ether, and a low yield of biphenyl (24) rather than the expected diphenyl ether. An analogous reaction is observed between the bromophenol and 3-methoxyphenol to afford (25) as a by-product, but not with 4-methoxyphenol or with a range of polyalkoxybenzenes.

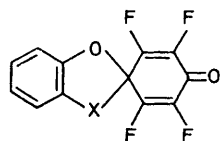
As polyhalogenophenoxy radicals are relatively inert,<sup>12</sup> the use of halogen substituents to minimise intermolecular coupling was next considered. Since the behaviour of polyfluorophenols in oxidative couplings had not been explored, syntheses of the diphenyl ether (26) and of the more accessible benzophenone (27) were carried out. The ketone was readily prepared by reaction of 4-methoxytetrafluorophenylmagnesium bromide with 2-methoxybenzaldehyde followed by oxidation of the alcohol and demethylation; the ether (26) was obtained by conversion of the bromo-compound (28) into the *t*-butyl ether (29) and subsequent dealkylation. Both (26) and (27) are oxidised to the dienones (30) or (31) in 11 and 8% yield, respectively, suggesting that the fluorine substituents had little beneficial effect in the formation of the dienone.



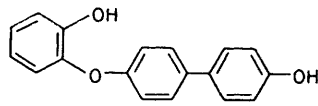
(24)  $R^1 = \text{OMe}; R^2 = \text{H}$   
(25)  $R^1 = \text{H}; R^2 = \text{OMe}$



(26)  $X = \text{O}; R^1 = R^2 = \text{OH}$   
(27)  $X = \text{CO}; R^1 = R^2 = \text{OH}$   
(28)  $X = \text{O}; R^1 = \text{OMe}, R^2 = \text{Br}$   
(29)  $X = \text{O}; R^1 = \text{OMe}, R^2 = \text{OBu}^t$



(30)  $X = \text{O}$   
(31)  $X = \text{CO}$

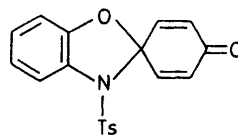


(32)

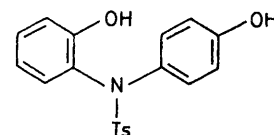
Active manganese dioxide was the most effective of a range of chemical oxidants in producing dienones, and no intramolecularly coupled product was obtained from anodic oxidation of any of the diphenol substrates under a variety of conditions. It seems that the formation of quinone monoacetals by phenolic coupling is most successful with derivatives of 1,4-benzoquinone and of 1,4-naphthoquinone. No dienone is obtained from the oxidation of 2,2'-dihydroxydiphenyl ether, or of the biphenyl (32). This may in part be due to the higher oxidation potential of the related quinonoid system

(although *p*-fluoranil derivatives can be obtained) or to the inherent instability of any dienone produced. It is, however, possible to prepare in reasonable yield the spirobenzoxazole (33) by manganese dioxide oxidation of the dihydroxydiphenylamine (34).

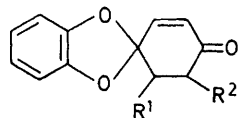
The dienone (17) shows considerable resistance to hydrolysis and prolonged treatment with methanolic hydrochloric acid gives, as well as diphenol (6), products (35) in which methanol has added to the acetal. In contrast to this when the dienones (18) and (19) are treated with sodium borohydride, spectral evidence is obtained for the formation of the corresponding dienols,



(33)



(34)



(35)  $R^1 = \text{H}, R^2 = \text{OMe}$   
or  $R^1 = \text{OMe}, R^2 = \text{H}$

but these are so readily hydrolysed with cleavage of the heterocyclic ring that they cannot be isolated in pure form. From reductive hydrolysis of the methyl dienone (18) the 4-methyldiphenol (8) is the major (75%) product, with the 5-methyl compound (7) the minor (25%), but with the nitrodienone (19) the ratio of derived 4-nitro-product (10) to 5-nitro-product (9) is reversed. Reduction of the spirobenzoxazole (33) yields exclusively the diphenylamine (34). It would appear that the dienols hydrolyse with liberation of the more acidic leaving group.

None of the spirodienones synthesised undergoes dienone-phenol rearrangements under the usual conditions for these reactions.

#### EXPERIMENTAL

I.r. spectra were recorded for potassium bromide discs with a Perkin-Elmer 137G spectrometer and <sup>1</sup>H n.m.r. spectra on a JEOL JNM C-60HL spectrometer with tetramethylsilane as the internal standard in deuteriochloroform unless otherwise indicated. <sup>19</sup>F N.m.r. spectra were determined by the Chemistry Department, University of Durham. Petroleum used had b.p. 60–80 °C.

*Preparation of 2,4'-Dihydroxydiphenyl Ethers (4).*—2,4'-Dimethoxy-3',5'-dimethyldiphenyl ether. 4-Bromo-2,6-dimethylanisole (64.5 g), 2-methoxyphenol (40 g), precipitated copper (20 g), pyridine (20 cm<sup>3</sup>), and anhydrous potassium carbonate (75 g) were heated together at 170 °C for 5 h. The cooled mixture was treated with dilute hydrochloric acid and extracted with ether. The extract was washed with sodium hydroxide solution, dried, concentrated, and distilled to give the ether (32 g), b.p. 197–199 °C at 12 mmHg, m.p. 35–37 °C (Found: C, 74.7; H, 7.2. C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>

requires C, 74.4; H, 7.0%;  $\tau$  7.75 (6 H, s,  $2 \times$  Me), 6.16, 6.32 (6 H,  $2 \times$  s,  $2 \times$  OMe), and 2.9–3.4 (6 H, m, aromatic). The ether (6 g) was heated at 190 °C for 2 h with pyridine hydrochloride (40 g). The cooled mixture was acidified with dilute hydrochloric acid, and the crude product dissolved in alkali and re-precipitated by acidification to give 2,4'-dihydroxy-3',5'-dimethyldiphenyl ether (15) (2.3 g), m.p. 130–131 °C (from benzene-petroleum) (Found: C, 73.1; H, 6.1.  $C_{14}H_{14}O_3$  requires C, 73.05; H, 6.1%),  $\tau$  7.85 (6 H, s,  $2 \times$  Me), 4.25, 5.5 (2 H,  $2 \times$  s,  $2 \times$  OH), and 3.0–3.35 (6 H, m, aromatic). 2,4'-Dimethoxy-2'-methyldiphenyl ether was prepared from 4-bromo-3-methylanisole as above; it was a colourless oil, b.p. 198–200 °C at 13 mmHg (Found: C, 74.0; H, 6.5.  $C_{15}H_{16}O_3$  requires C, 73.8; H, 6.5%),  $\tau$  7.80 (3 H, s, Me), 6.26, 6.38 (6 H,  $2 \times$  s,  $2 \times$  OMe), 3.1–3.5 (7 H, m, aromatic). To a solution of the methyl ether (15 g) in pyridine (200 cm<sup>3</sup>) and water (100 cm<sup>3</sup>) was added potassium permanganate (19.2 g) and the mixture was heated under reflux for 2 h, and filtered through Celite; the cooled filtrate was acidified with concentrated hydrochloric acid, extracted with ether, and the extract treated with aqueous sodium hydroxide solution, which on acidification gave 2,4'-dimethoxy-2'-carboxydiphenyl ether (5.0 g), m.p. 89–90 °C (from benzene-petroleum) (Found: C, 66.0; H, 5.0.  $C_{15}H_{14}O_5$  requires C, 65.7; H, 5.1%;  $\tau$  6.20 (6 H, s,  $2 \times$  OMe), 2.3–3.3 (7 H, m, aromatic), and –0.7 (1 H, s, CO<sub>2</sub>H). Pyridine hydrochloride demethylation of the previous compound (7.6 g) gave 2,4'-dihydroxy-2'-carboxydiphenyl ether (6.2 g), m.p. 182–183 °C (from water) (Found: C, 63.7; H, 4.4.  $C_{13}H_{10}O_5$  requires C, 63.4; H, 4.1%). This acid by reaction with methanol and acetyl chloride gave 2,4'-dihydroxy-2'-methoxycarbonyldiphenyl ether (14), m.p. 98–99 °C (from benzene-petroleum) (Found: C, 64.4; H, 4.5.  $C_{14}H_{12}O_5$  requires C, 64.6; H, 4.6%;  $\tau$  6.14 (3 H, s, OMe), 2.7–3.2 (7 H, m, aromatic), and 2.2, 3.5 (2 H,  $2 \times$  s,  $2 \times$  OH).

Permanganate oxidation of 2,4'-dimethoxy-4-methyldiphenyl ether<sup>9</sup> as described above gave 2,4'-dimethoxy-4-carboxydiphenyl ether, m.p. 172–173 °C (from benzene) (Found: C, 65.5; H, 5.2.  $C_{15}H_{14}O_5$  requires C, 65.7; H, 5.1%;  $\tau$  6.05, 6.20 (6 H, s  $\times$  s,  $2 \times$  OMe), and 2.30–3.35 (7 H, m, aromatic). Demethylation yielded 2,4'-dihydroxy-4-carboxydiphenyl ether, m.p. 201–202 °C (from water) (Found: C, 63.3; H, 4.1.  $C_{13}H_{10}O_5$  requires C, 63.4; H, 4.1%). On esterification of this compound was obtained 2,4'-dihydroxy-4-methoxycarbonyldiphenyl ether (12), m.p. 144–145 °C (from benzene) (Found: C, 64.9; H, 4.4.  $C_{14}H_{12}O_5$  requires C, 64.6; H, 4.6%;  $\tau$  6.14 (3 H, s, OMe). Similarly from 2,4'-dimethoxy-5-methyldiphenyl ether<sup>9</sup> were prepared: 2,4'-dimethoxy-5-carboxydiphenyl ether, m.p. 182–184 °C (from chloroform) (Found: C, 65.5; H, 5.4.  $C_{15}H_{14}O_5$  requires C, 65.7; H, 5.1%;  $\tau$  6.1, 6.22 (6 H, s,  $2 \times$  OMe), and 2.1–3.2 (7 H, m, aromatic); 2,4'-dihydroxy-5-carboxydiphenyl ether, m.p. 209–211 °C (from water) (Found: C, 63.2; H, 3.9.  $C_{13}H_{10}O_5$  requires C, 63.4; H, 4.1%); and 2,4'-dihydroxy-5-methoxycarbonyldiphenyl ether (11), m.p. 129–130 °C (from benzene) (Found: C, 64.3; H, 4.5.  $C_{14}H_{12}O_5$  requires C, 64.6; H, 4.6%;  $\tau$  6.15 (3 H, s, OMe), and 2.2–3.2 (7 H, m, aromatic). 2,4-Dimethoxy-4-nitrodiphenyl ether, was prepared as above from 2-bromo-5-nitroanisole (46 g) with the reaction mixture being heated for 2 h, and the product purified by chromatography [silica gel, eluant chloroform–light petroleum (1:1): the ether (23 g) had m.p. 110 °C (from ethanol) (Found: C, 60.9; H, 4.9; N, 5.0.  $C_{14}H_{13}NO_5$  requires C, 61.1; H, 4.7; N,

5.1%;  $\tau$  6.02, 6.20 (6 H,  $2 \times$  s,  $2 \times$  OMe), and 2.20–3.40 (7 H, m, aromatic). Treatment of this compound with pyridine hydrochloride yielded 2,4'-dihydroxy-4-nitrodiphenyl ether (10), m.p. 169–170 °C (from benzene) (Found: C, 58.7; H, 3.8; N, 5.6.  $C_{12}H_9NO_5$  requires C, 58.3; H, 3.6; N, 5.7%). 2,4'-Dimethoxy-2'-nitrodiphenyl ether was obtained from 4-bromo-3-nitroanisole as above, with cupric oxide in place of copper; it had m.p. 70–71 °C (from ethanol) (Found: C, 61.4; H, 4.5; N, 4.9.  $C_{14}H_{13}NO_5$  requires C, 61.1; H, 4.7; N, 5.1%;  $\tau$  6.16 (3 H, s, OMe), and 2.5–3.3 (7 H, m, aromatic). The ether, on demethylation, yielded 2,4'-dihydroxy-2'-nitrodiphenyl ether (13), m.p. 146–148 °C (from chloroform) (Found: C, 58.6; H, 3.7; N, 5.7.  $C_{12}H_9NO_5$  requires C, 59.1; H, 3.6; N, 5.7%). 2,4-Dimethoxy-5-nitrodiphenyl ether had m.p. 109–110 °C (from ethanol) (Found: C, 61.5; H, 4.8; N, 5.3.  $C_{14}H_{13}NO_5$  requires C, 61.1; H, 4.7; N, 5.1%;  $\tau$  6.01, 6.20 (6 H,  $2 \times$  s,  $2 \times$  OMe), and 1.95–3.05 (7 H, m, aromatic).

2,4'-Dihydroxy-2',3',5',6'-tetrafluorobenzophenone (27).—A solution of 4-bromotetrafluoroanisole (37.5 g) in dry tetrahydrofuran (50 cm<sup>3</sup>) was added during 0.5 h to an ice-cooled mixture of magnesium turnings (4.25 g) in tetrahydrofuran (150 cm<sup>3</sup>). To the resulting brown solution was added 2-methoxybenzaldehyde (20.5 g) in tetrahydrofuran (75 cm<sup>3</sup>). After 2 h stirring, the usual hydrolytic procedures gave (2-methoxyphenyl)-4-methoxy-2,3,5,6-tetrafluorophenyl-methanol (37 g) as colourless prisms, m.p. 93–94 °C (from chloroform-petroleum) (Found: C, 57.3; H, 3.5; F, 24.5.  $C_{15}H_{12}F_4O_3$  requires C, 57.0; H, 3.8; F, 24.0%;  $\nu_{\max}$  3480 cm<sup>–1</sup> (OH);  $\tau$  6.47 (1 H, d, CH–OH), 6.0, 6.24 (6 H,  $2 \times$  s,  $2 \times$  OMe), 3.72 (1 H, CHOH), and 2.4–3.3 (4 H, m, aromatic). The alcohol (10 g) in benzene (150 cm<sup>3</sup>) was heated under reflux for 3 h with active manganese dioxide. The mixture was filtered through Celite, and the filtrate evaporated to give 2,4'-dimethoxy-2',3',5',6'-tetrafluorobenzophenone (9 g), m.p. 86–87 °C (from chloroform-petroleum) (Found: C, 57.0; H, 3.3; F, 24.6.  $C_{15}H_{10}F_4O_3$  requires C, 57.3; H, 3.2; F, 24.2%;  $\nu_{\max}$  1645 cm<sup>–1</sup> (CO);  $\tau$  5.87; 6.30 (6 H,  $2 \times$  s,  $2 \times$  OMe), and 2.20–3.20 (4 H, m, aromatic). The benzophenone (6 g), anhydrous aluminium chloride (12 g), and benzene were heated together at 120 °C for 2 h, the cooled mixture treated with ice then dilute hydrochloric acid, and the resulting precipitate collected to give 2,4'-dihydroxy-2',3',5',6'-tetrafluorobenzophenone (3 g), m.p. 190–191 °C (from benzene) (Found: C, 54.8; H, 2.3; F, 27.1.  $C_{13}H_6F_4O_3$  requires C, 54.5; H, 2.1; F, 26.0%;  $\nu_{\max}$  3200 (OH) 1660 and 1615 cm<sup>–1</sup> (CO).

2,4'-Dihydroxy-2',3',5',6'-tetrafluorodiphenyl Ether (26).—Pentafluorobromobenzene (54 g), sodium 2-methoxyphenoxide (31 g), and dry dimethylformamide (250 cm<sup>3</sup>) were stirred together at 105 °C for 13 h; the cooled mixture was then poured into water, the resulting precipitate collected, and the filtrate extracted with petroleum. The extract was evaporated, and the residue, combined with the precipitate, gave 2-methoxy-4'-bromo-2',3',5',6'-tetrafluorodiphenyl ether (28) (69 g), m.p. 68–69 °C (from petroleum) (Found: C, 44.6; H, 1.9; halogen 43.9.  $C_{13}H_2BrF_4O_2$  requires C, 44.4; H, 2.0; halogen 44.4%;  $\tau$  6.14 (3 H, s, MeO), and 2.8–3.2 (4 H, m, aromatic);  $\delta_F$  ( $C_6F_5$  standard) two multiplets of equal intensity at 8.2 (F *ortho* to OAr) and 27.8 (F *ortho* to Br). This bromo-compound (110 g) in dry ether (250 cm<sup>3</sup>) was added to magnesium turnings (10.5 g) in ether (100 cm<sup>3</sup>); the mildly exothermic reaction was initiated with dibromoethane. To the resulting dark solution, with stirring, was added t-butyl perbenzoate (80 g)



in ether (150 cm<sup>3</sup>) so that the mixture boiled gently. After 12 h, the reaction mixture was subjected to acid hydrolysis, and the ether layer was separated, washed with dilute acid and alkali, dried, evaporated, and the residue dissolved in benzene-petroleum (1 : 9) and passed down a silica column in the same solvent. After unreacted bromo-compound there was obtained crude 2-methoxy-4'-t-butoxy-2',3',5',6'-tetrafluorodiphenyl ether (29), a portion of which on crystallisation (from petroleum) had m.p. 70–71 °C (Found: C, 59.5; H, 4.4. C<sub>17</sub>H<sub>16</sub>F<sub>4</sub>O<sub>3</sub> requires C, 59.3; H, 4.7%);  $\tau$  8.60 (9 H, s, Bu<sup>t</sup>O), and 2.90–3.3 (4 H, m, aromatic). The t-butyl ether was heated at 160 °C for 2 min with a little toluene-*p*-sulphonic acid, the cooled residue dissolved in aqueous sodium hydroxide, and the filtered solution acidified to give 2-methoxy-4'-hydroxy-2',3',5',6'-tetrafluorodiphenyl ether (29.7 g) as plates, m.p. 126–127 °C (from petroleum) (Found: C, 54.6; H, 2.9; F, 26.0. C<sub>13</sub>H<sub>8</sub>F<sub>4</sub>O<sub>3</sub> requires C, 54.2; H, 2.8; F, 26.4%);  $\tau$  6.07 (3 H, s, MeO), 4.20 (1 H, br s, OH), and 2.80–3.35 (4 H, m, aromatic). This compound (15 g) on demethylation with anhydrous aluminium chloride (30 g) in benzene (30 cm<sup>3</sup>) as described above gave the *title ether* (9.7 g), m.p. 135–136 °C (from benzene-petroleum) (Found: C, 52.65; H, 2.2. C<sub>12</sub>H<sub>6</sub>F<sub>4</sub>O<sub>3</sub> requires C, 52.55; H, 2.2%).

**2-Hydroxyphenyl 4'-Hydroxybiphenyl-4-yl Ether (32).**—Reaction of 4-bromo-4'-methoxybiphenyl (52 g) with 2-methoxyphenol (40 g) as before yielded 2-methoxyphenyl 4'-methoxybiphenyl-4-yl ether (34 g), m.p. 101–102 °C (from petroleum) (Found: C, 78.2; H, 6.0. C<sub>20</sub>H<sub>18</sub>O<sub>3</sub> requires C, 78.4; H, 5.9%);  $\tau$  6.20 (6 H, 2  $\times$  s, 2  $\times$  OMe), and 2.50–3.17 (12 H, m, aromatic). Demethylation of this compound with pyridine hydrochloride at 230 °C for 2 h yielded the *diphenolic ether* (33), m.p. 162–163 °C (from benzene) (Found: 77.7; H, 4.8. C<sub>18</sub>H<sub>14</sub>O<sub>3</sub> requires C, 77.7; H, 5.09%).

**Preparation of Spirobenzodioxoles.**—The appropriate 2,4'-dihydroxydiphenyl ether (1 part), active manganese dioxide <sup>13</sup> (5 parts), and benzene (100 parts) were heated together under Dean and Stark conditions until starting material disappeared (t.l.c. examination). The mixtures were filtered through Celite, concentrated, and passed down silica columns in benzene or chloroform to separate the products from tars and benzoquinone; the dienones appeared in the first fraction of eluate. In this way were obtained: 4-nitro-1,3-benzodioxole-2-spirocyclohexadien-4'-one (19), m.p. 175–176 °C (from benzene-petroleum) (Found: C, 58.5; H, 3.2; N, 5.5. C<sub>12</sub>H<sub>7</sub>NO<sub>5</sub> requires C, 58.8; H, 2.9; N, 5.7%); methyl 4'-oxo-1,3-benzodioxole-2-spirocyclohexadiene-4-carboxylate (20), m.p. 115–116 °C (from methanol) (Found: C, 65.4; H, 4.1. C<sub>14</sub>H<sub>10</sub>O<sub>5</sub> requires C, 65.1; H, 3.9%); methyl 4'-oxo-1,3-benzodioxole-2-spirocyclohexadiene-2'-carboxylate (22), m.p. 138–140 °C (from benzene-petroleum) (Found: C, 65.4; H, 4.0. C<sub>14</sub>H<sub>10</sub>O<sub>5</sub> requires C, 65.1; H, 3.9%); 3',5'-dimethyl-1,3-benzodioxole-2-spirocyclohexadien-4'-one (23), m.p. 124–125 °C (from petroleum) (Found: C, 73.9; H, 5.6. C<sub>14</sub>H<sub>12</sub>O<sub>3</sub> requires C, 73.7; H, 5.3%); 2'-nitro-1,3-benzodioxole-2-spirocyclohexadien-4'-one (21) (Found: *m/e* 245. C<sub>12</sub>H<sub>7</sub>NO<sub>5</sub> requires *m/e* 245). The i.r. spectra of all these compounds showed peaks at 1 695–1 670 and at 1 660–1 640 cm<sup>-1</sup>, (dienones); dienone vinylic protons are at  $\tau$  ca. 3.1 and 3.7 (*J* 10 Hz where appropriate). 2',3',5',6'-Tetrafluoro-1,3-benzodioxole-2-spirocyclohexadien-4'-one (30), m.p. 126–127 °C (from petroleum) (Found: C, 53.3; H, 1.3%; *m/e* 272.008 7. C<sub>12</sub>H<sub>4</sub>F<sub>4</sub>O<sub>3</sub> requires C, 52.9; H, 1.5%; *m/e* 272.009 6);  $\nu_{\max}$  1 700, 1 708 cm<sup>-1</sup> (dienone);  $\delta_F$ , two

singlets of equal intensity at 7.26 and 19.95 (downfield of C<sub>6</sub>F<sub>6</sub>).

2',3',5',6'-Tetrafluorobenzofuran-2-spirocyclohexadiene-3,4'-dione (31). This had m.p. 160 °C (from carbon tetrachloride) (Found: C, 55.1; H, 1.45; F, 27.3%; *m/e* 284. C<sub>13</sub>H<sub>4</sub>F<sub>4</sub>O<sub>3</sub> requires C, 54.9; H, 1.4; F, 26.8%; *m/e* 284);  $\nu_{\max}$  1 785, 1 770 cm<sup>-1</sup> (C=O), 1 709, 1 695, 1 620, and 1 597 cm<sup>-1</sup> (dienone);  $\delta_F$  two doublets of equal intensity at 7.7 (F *ortho* to C=O) and 25.5 (downfield of C<sub>6</sub>F<sub>6</sub>).

**Preparation of Spirobenzoxazole (33).**—*N*-2-benzyloxyphenyl-*N*-4-benzyloxyphenyltoluene-4-sulphonamide <sup>14</sup> (4 g) and palladium-charcoal (5%, 1 g) in dioxan (200 cm<sup>3</sup>) containing concentrated hydrochloric acid (5 cm<sup>3</sup>) was shaken at 80 °C under hydrogen (4 atm). When uptake of hydrogen ceased, the mixture was filtered, the filtrate evaporated, the residue dissolved in sodium hydroxide, and the filtered solution acidified to give *N*-2-hydroxyphenyl-*N*-4-hydroxyphenyltoluene-4-sulphonamide (34) (2 g), m.p. 176–177 °C (from ethyl acetate-petroleum) (Found: C, 63.8; H, 5.0; N, 3.7. C<sub>19</sub>H<sub>17</sub>NO<sub>4</sub>S requires C, 64.1; H, 4.8; N, 3.9%);  $\nu_{\max}$  3 420, 3 360 cm<sup>-1</sup> (2  $\times$  OH);  $\tau$  ([<sup>2</sup>H<sub>6</sub>]DMSO) 7.57 (3 H, s, Me), and 2.56–3.51 (12 H, m, aromatic). This diphenol (2.4 g) in benzene (150 cm<sup>3</sup>) was heated under reflux for 4 h with manganese dioxide (24 g), the filtered solution evaporated, and the residue recrystallised (from ethyl acetate-petroleum) to afford 3-(*p*-tolylsulphonyl)-2,3-dihydro-1,3-benzoxazole-2-spirocyclohexadien-4'-one (33), (1.1 g, 46%), m.p. 172–173 °C (decomp.) (Found: C, 64.5; H, 4.5; N, 3.8. C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub>S requires C, 64.6; H, 4.3; N, 4.0%)  $\nu_{\max}$  1 682, 1 645, and 1 613 cm<sup>-1</sup> (dienone);  $\tau$  7.65 (3 H, s, Me), 3.38, 3.5, 3.8, and 3.93 (4 H, q, vinylic). Only active manganese dioxide prepared by the method of ref. 15 consistently gave reasonable yield of dienone.

**Arylation of Phenols.**—2,6-Di-*t*-butyl-4-bromophenol (28.5 g), 3-methoxyphenol (12.4 g), activated copper (6 g), anhydrous potassium carbonate (30 g), and dry pyridine (6 cm<sup>3</sup>) were heated together at 180 °C for 4 h. The dark mixture was treated with hydrochloric acid and extracted with ether. The ether extract was washed with acid and water, dried, evaporated, and the residual gum in toluene applied to a silica column. Elution with petroleum yielded unreacted bromophenol, 3,3',5,5'-tetrabutylidiphenylquinone, and 4,4'-dihydroxy-3,3',5,5'-tetrabutylbiphenyl; subsequent elution with toluene gave 3,5-di-*t*-butyl-4,4'-(or 2')-dihydroxy-2'-(or 4')-methoxybiphenyl (25) (1.7 g, 5%), m.p. 128–129 °C (from petroleum) (Found: C, 76.9; H, 8.8. C<sub>21</sub>H<sub>28</sub>O<sub>3</sub> requires C, 76.8; H, 8.5%);  $\nu_{\max}$  3 620 cm<sup>-1</sup> (OH flanked by *t*-butyl) and 3 415 cm<sup>-1</sup> (OH);  $\tau$  8.83 (18 H, 2 s, 2  $\times$  *t*-Bu), 6.87 (3 H, s, OMe), 5.54 and 5.63 (2 H, 2  $\times$  s, D<sub>2</sub>O exchangeable, 2  $\times$  OH), and 3.65–4.05 (5 H, m, aromatics). When the above reaction was attempted at 100 °C, no biphenyl was formed; reaction in *NN*-diethylacetamide at 150 °C or in *N*-methylpyrrolidone at 185 °C gave very complex mixtures of products. From the reaction of 2-methoxyphenol with the bromophenol under the above conditions was isolated 3,5-di-*t*-butyl-4,2'-(or 4')-dihydroxy-3'-methoxybiphenyl (24) (8%), m.p. 159–160 °C (from petroleum) (Found: C, 77.1; H, 8.3. C<sub>21</sub>H<sub>28</sub>O<sub>3</sub> requires C, 76.8; H, 8.5%);  $\nu_{\max}$  3 620 and 3 545 cm<sup>-1</sup> (OH);  $\tau$  8.51 (18 H, s, 2  $\times$  *t*-Bu), 6.08 (3 H, s, MeO), 4.41 and 4.82 (2 H, 2  $\times$  s, 2  $\times$  OH), and 2.72–3.05 (5 H, m, aromatic). Reaction of 4-methoxyphenol with the dibutylbromophenol afforded no biphenyl, but from the product mixture was isolated 3,5-di-*t*-butyl-4-hydroxy-4'-methoxydiphenyl ether (3%), m.p. 95–96 °C (from petroleum) (Found:

C, 76.2; H, 8.7.  $C_{21}H_{28}O_3$  requires C, 76.8; H, 8.5%;  $\nu_{\max}$ , 3'630  $\text{cm}^{-1}$  (OH);  $\tau$  8.85 (18 H, s,  $2 \times \text{Bu}^t$ ), 6.88 (3 H, s, MeO), 5.92 (1 H, s,  $\text{D}_2\text{O}$  exchangeable, OH), and 4.23—4.39 (6 H, m, aromatic).

**Hydrolysis of Dienone (20).**—A solution of the dienone (2 g) in methanol (250  $\text{cm}^3$ ) and concentrated hydrochloric acid (75  $\text{cm}^3$ ) was heated under reflux for 1 h, concentrated to small volume under reduced pressure, the residue extracted with benzene, and the extract washed and concentrated. T.l.c. examination (silica gel, toluene) showed the reaction product to be a complex mixture, which yielded the following components on repeated column and preparative layer chromatography: (a) unreacted dienone (20); (b) *dienone-methanol adduct* (35), m.p. 113—115 °C (from benzene-petroleum) (Found:  $m/e$  232.073 562.  $C_{13}H_{12}O_4$  requires  $M$ , 232.073 552);  $\nu_{\max}$ , 1 695  $\text{cm}^{-1}$  (CO) and 1 634  $\text{cm}^{-1}$  (C=C) [the i.r. spectrum of (20) has peaks at 1 675 and 1 640  $\text{cm}^{-1}$ ]; and (c) 2,4'-dihydroxydiphenyl ether (6), and mono- and di-chloro-substituted derivatives (mass-spectral evidence).

**Reaction of Dienones with Sodium Borohydride.**—The methyl dienone (18) (400 mg) in methanol (20  $\text{cm}^3$ ) and water (5  $\text{cm}^3$ ) was treated with portions of sodium borohydride till a colourless solution was obtained. The reaction mixture was evaporated under reduced pressure, the residue dissolved in ether, and the solution washed, dried, and evaporated to give a colourless solid (370 mg). Examination of the methyl proton resonances in the n.m.r. spectrum ( $\text{CDCl}_3$ - $[\text{H}_5]$ pyridine) showed that this solid consisted of 4-methyl compound (8) (75%) and 5-methyl isomer (7) (25%). Similar reaction of nitrodienone (19) (400 mg) with sodium borohydride yielded a product (350 mg) which was methylated with diazomethane to give a mixture of nitrodiphenyl ethers; this mixture was shown by n.m.r. [ $(\text{CDCl}_3$ ;  $\text{Eu}(\text{fod})_3$  addition] to consist of the dimethyl ether of the 4-nitro-compound (10) (30%) and of the 5-nitro-compound (9) (70%). From the reaction of dienone (33) with sodium borohydride in ethanol was obtained the dihydroxy-

diphenylamine (34) (86%), identical (i.r. spectrum, mixed m.p.) with the authentic compound.

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