

## Reactions of Quinones with Aromatic Ethers. Part III.<sup>1</sup> Arylbenzoquinones and Dibenzofurans from 2,5- and 2,6-Dichlorobenzoquinone and Veratrole

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2,5-Dichlorobenzoquinone reacts with veratrole in 70% v/v aqueous sulphuric acid to form 2,5-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (III; X = H, Y = Cl), 2,5-dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl], and 1,4-dichloro-7,8-dimethoxydibenzofuran-2-ol (IV; X = H, Y = Cl). Similar reactions with 2,6-dichlorobenzoquinone give 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone [III; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], 1,3-dichloro-7,8-dimethoxydibenzofuran-2-ol (IV; X = Cl, Y = H), and 1,3-dichloro-7,8-dimethoxy-4-(3,4-dimethoxyphenyl)dibenzofuran-2-ol [IV; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]. In both cases the veratrole oxidation products 2,3,6,7,10,11-hexamethoxytriphenylene (I) and 2,5,6,9,12,13-hexamethoxydibenzo[fg,op]naphthacene-1,10-quinone (II) are also obtained. The dibenzofurans result from the acid-catalysed cyclisation of the corresponding arylbenzoquinones; similar cyclisations can be effected by visible light.

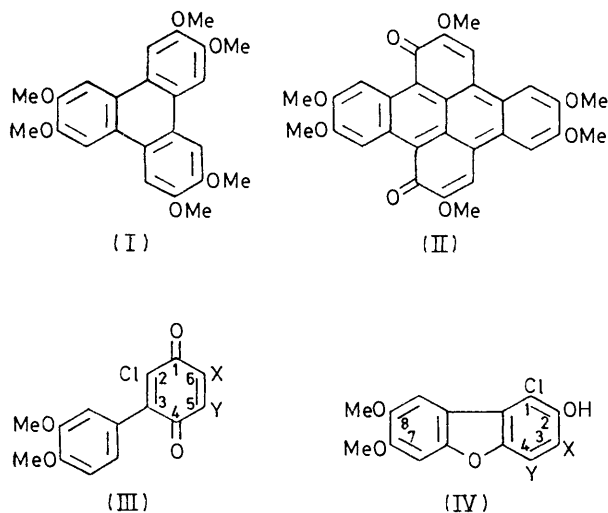
FULLY substituted benzoquinones such as chloranil oxidise veratrole in aqueous sulphuric acid giving the triphenylene (I) and the dibenzonaphthacene-1,10-quinone (II).<sup>1</sup> This paper describes the products from related reactions with 2,5- and 2,6-disubstituted benzoquinones.

2,5-Dichlorobenzoquinone reacted with an excess of veratrole in 70% v/v aqueous sulphuric acid to give 2,5-dichlorohydroquinone and some (33%) triphenylene (I) as expected. Arylation of the quinone also occurred, with formation of a mixture of quinols which, after oxidation by air or iron(III) chloride, gave the arylquinone (III; X = H, Y = Cl) (50%) and the diarylquinone [III;

matic protons, one phenolic hydroxy-proton, and six methoxy-protons; we formulate it accordingly as the dibenzofuran (IV; X = H, Y = Cl). It appears that the quinol formed by acid-catalysed addition of veratrole to the dichlorobenzoquinone is oxidised by the excess of the latter. The resulting arylquinone (III; X = H, Y = Cl) then either undergoes further arylation and oxidation to give the diarylquinone [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl], or cyclises to form the dibenzofuran (IV; X = H, Y = Cl). To confirm that the last reaction is acid-catalysed we treated the arylquinone with 70% v/v aqueous sulphuric acid overnight and obtained the dibenzofuran in 88% yield. The cyclisation presumably involves initial protonation of the C-1 oxygen atom of the quinone (III; X = H, Y = Cl) and subsequent attack (either nucleophilic or electrophilic) by the C-4 oxygen atom on the aromatic nucleus. The cyclisation of arylbenzoquinones in this way under acidic conditions has not previously been reported though similar reactions have been effected both photochemically<sup>3</sup> and thermally.<sup>4</sup>

The diarylquinone [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] did not undergo the acid-catalysed reaction, presumably because of its low solubility in 70% v/v aqueous sulphuric acid, and we sought an alternative route to the corresponding dibenzofuran. We had noticed that a solution of the arylquinone (III; X = H, Y = Cl) in chloroform became nearly colourless on prolonged exposure to visible light and found the photoproduct to be the dibenzofuran (IV; X = H, Y = Cl). The exposure of the diarylquinone [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] in chloroform solution to visible light resulted in a similar reaction to give the desired dibenzofuran [IV; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl]. Surprisingly, little or no reaction occurred in either case when acetonitrile<sup>3</sup> was used as solvent.

The reactions between 2,6-dichlorobenzoquinone and veratrole in 70% aqueous sulphuric acid gave products closely related to those already described. The use of an excess of veratrole gave the triphenylene (I) (39%), the



X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] (13%). The reaction between veratrole and an excess of 2,5-dichlorobenzoquinone took a different course. Although the triphenylene (I) (17%) was again obtained, together with a trace of the dibenzonaphthacene-1,10-quinone (II), the diarylquinone [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] (38%) and a colourless phenol C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> (38%) were the major products. The u.v. absorption of the phenol resembles that<sup>2</sup> of dibenzofuran and its n.m.r. spectrum shows the presence of three apparently uncoupled ar-

<sup>1</sup> Part II, O. C. Musgrave and C. J. Webster, *J. Chem. Soc. (C)*, 1971, 1397.

<sup>2</sup> 'U.V. Atlas of Organic Compounds,' Butterworths, London, 1967, Spectrum H14/1.

<sup>3</sup> H. J. Hageman and W. G. B. Huysmans, *Chem. Comm.*, 1969, 837.

<sup>4</sup> H. J. Hageman and U. E. Wiersum, *Chem. Comm.*, 1971, 497.

dibenzonaphthacene-1,10-quinone (II) (7%), 2,6-dichlorohydroquinone, and small amounts of the diarylbenzoquinone [III; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (4%) and the dibenzofuran (IV; X = Cl, Y = H) (2%). With an excess of the dichlorobenzoquinone similar yields of the triphenylene (I) (37%) and the dibenzonaphthacenequinone (II) (8%) resulted, together with the dibenzofurans (IV; X = Cl, Y = H) (6%) and [IV; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (14%). The structures of these dibenzofurans follow from their solubility in aqueous alkali, the general resemblance of their light absorptions to those of the dibenzofurans (IV; X = H, Y = Cl) and [IV; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl], and their formation in good yield when the arylbenzoquinones (III; X = Cl, Y = H) and [III; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], respectively, were treated overnight with 70% v/v aqueous sulphuric acid.

In the mass spectrometer the dibenzofuran (IV; X = H, Y = Cl) gives rise to several prominent ions, the most abundant being those formed by loss of CH<sub>3</sub>• followed by CICO• (or CO and Cl•) from the molecular ion. The mass spectra of the closely related dibenzofurans [IV; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] and [IV; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] are virtually identical, as would be expected. Little fragmentation occurs, the only conspicuous ion being formed from the molecular ion by loss of CH<sub>3</sub>• and CICO• in each case.

We prepared authentic specimens of the arylquinones (III; X = H, Y = Cl) and [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl], and (III; X = Cl, Y = H) and [III; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] by treating<sup>5</sup> 2,5-dichlorobenzoquinone and 2,6-dichlorobenzoquinone, respectively, with buffered solutions of 3,4-dimethoxybenzenediazonium chloride at 0°.

#### EXPERIMENTAL

Details of the general methods and of the instruments used were given in Part I.<sup>6</sup> U.v. spectra were measured for ethanolic solutions unless stated otherwise; mass spectra were measured with an A.E.I. MS30 spectrometer. The term '70% v/v aqueous sulphuric acid' used in this and previous Parts refers to an aqueous solution 100 ml of which contains 70 ml of concentrated sulphuric acid.

*Reaction of 2,5-Dichloro-1,4-benzoquinone with Veratrole.*—(a) *Excess of the quinone.* A mixture of veratrole (0.55 g, 0.004 mol), powdered 2,5-dichlorobenzoquinone (1.87 g, 0.01 mol), and 70% v/v aqueous sulphuric acid (25 ml) was shaken for 30 min, kept at room temperature for 7 days, and diluted with water (50 ml). The purple-red precipitate (1.83 g) was collected, washed with water, and dried, and a solution of this (500 mg) in chloroform–benzene (4 : 1 v/v) was filtered through a column of silica gel. Elution with the same solvent afforded unchanged 2,5-dichlorobenzoquinone (150 mg) followed by a red solid (260 mg). A small amount of 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,10-quinone (II)<sup>1</sup> remained at the top of the column as a purple band. A solution of the red solid in chloroform (50 ml) was shaken with aqueous m-sodium hydroxide (3 × 30 ml). Acidification of the aqueous layer and extraction with ether gave 1,4-dichloro-7,8-dimethoxydibenzofuran-2-ol (IV;

X = H, Y = Cl) (130 mg, 38%) which crystallised from methanol as needles, m.p. 224.5–225° [Found: C, 53.7; H, 3.4; Cl, 22.1; OMe, 19.7%; *M* (by vapour pressure osmometry in acetone), 325. C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> requires C, 53.7; H, 3.2; Cl, 22.65; 2 OMe, 19.8%; *M*, 313.1], *v*<sub>max</sub> 3400 cm<sup>-1</sup> (OH), *λ*<sub>max</sub> (MeOH) 233 (log *ε* 4.36), 264 (4.04), and 308 nm (4.35), *λ*<sub>inf</sub> 245 (4.17), 256 (3.99), 298 (4.24), 318 (4.21), and 327 nm (4.03), *δ* 7.66, 7.15, and 7.09 (each 1H, sharp s; H-9, H-3, and H-6), 5.48 (1H, sharp s, ArOH), and 4.00 and 3.98 (each 3H, s, ArOCH<sub>3</sub>), *m/e* 312 (100%; *M*<sup>+</sup>), 297 (35%; *M* – CH<sub>3</sub>), 269 (13%, 297 – CO), 254 (18%, 269 – CH<sub>3</sub>), 234 (71%, 297 – COCl and 269 – Cl), 226 (18%, 254 – CO), and 156 (9%, *M*<sup>2+</sup>). Evaporation of the chloroform solution gave the alkali-insoluble fraction, which was extracted repeatedly with boiling acetone. Evaporation of the filtrate and crystallisation of the residue from chloroform afforded 2,3,6,7,10,11-hexamethoxytriphenylene (I) (25 mg, 17%), m.p. 316–317° (lit.,<sup>1</sup> 317.5–318.5°). The acetone-insoluble solid crystallised from chloroform–acetone to give 2,5-dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone [III; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] as deep red rhombohedra (92 mg, 38%), m.p. 306.5–307.5° (Found: C, 59.0; H, 4.3; Cl, 16.3; OMe, 27.7. C<sub>22</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>6</sub> requires C, 58.8; H, 4.05; Cl, 15.8; 4 OMe, 27.65%), *v*<sub>max</sub> 1670 cm<sup>-1</sup> (quinone C=O), *λ*<sub>max</sub> (CHCl<sub>3</sub>) 266 (log *ε* 4.35), 280.5 (4.40), 367 (3.26), and 486 nm (3.57).

(b) *Excess of veratrole.* A mixture of veratrole (1.80 g, 0.013 mol), powdered 2,5-dichlorobenzoquinone (0.94 g, 0.005 mol), and 70% v/v aqueous sulphuric acid (15 ml) was shaken for 30 min, kept at room temperature for 7 days, diluted with water (20 ml), and filtered. The filtrate slowly deposited crystals of 2,5-dichlorohydroquinone (0.13 g, m.p. 169–170° (lit.,<sup>7</sup> 172°). Part (0.20 g) of the insoluble pale purple residue (1.83 g) was heated at 70° and 0.05 mmHg to remove more 2,5-dichlorohydroquinone (11 mg), and a solution of the residue in chloroform was filtered through a short column of silica gel to remove coloured materials. The nearly colourless eluate became deep red when shaken with aqueous m-sodium hydroxide and evaporation of the chloroform layer gave a red solid (45 mg) which was extracted repeatedly with boiling acetone to remove 2,3,6,7,10,11-hexamethoxytriphenylene (26 mg, 33%). Crystallisation of the residue from chloroform–acetone gave 2,5-dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone as deep red crystals (17 mg, 13%), m.p. 301–302°. The alkaline aqueous layer was acidified and shaken with chloroform. Anhydrous iron(III) chloride was added to the nearly colourless chloroform layer and the resulting solution was washed with 2*M*-hydrochloric acid. Evaporation left 2,5-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (III; X = H, Y = Cl) (90 mg, 50%) as red crystals, m.p. 177–178° (Found: C, 53.7; H, 3.4; Cl, 21.9; OMe, 19.6. C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> requires C, 53.7; H, 3.2; Cl, 22.65; 2 OMe, 19.8%), *v*<sub>max</sub> 1675 cm<sup>-1</sup> (quinone C=O), *λ*<sub>max</sub> 274 (log *ε* 4.20) and 487 nm (3.12), *λ*<sub>inf</sub> 266 (4.19) and 330 nm (2.92); *λ*<sub>max</sub> (MeCN) 263 (4.24), 272 (4.27), 330 (2.83), and 485 nm (3.10); *λ*<sub>max</sub> (CHCl<sub>3</sub>) 276 (4.30), 335 (2.90), and 514 (3.22), *λ*<sub>inf</sub> 268 nm (4.26).

*Reaction of 2,6-Dichloro-1,4-benzoquinone with Veratrole.*—

(a) *Excess of the quinone.* A mixture of powdered 2,6-dichlorobenzoquinone (2.65 g, 0.015 mol), veratrole (1.0 g, 0.007 mol), and 70% v/v aqueous sulphuric acid (20 ml) was

<sup>5</sup> Cf. D. E. Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478; B. F. Cain, *J. Chem. Soc.*, 1961, 936.

<sup>6</sup> O. C. Musgrave and C. J. Webster, *J. Chem. Soc. (C)*, 1971, 1393.

<sup>7</sup> A. R. Ling, *J. Chem. Soc.*, 1892, **61**, 558.

shaken for 30 min, kept at room temperature for 1 week, and diluted with water (50 ml). The resulting purple solid (2.62 g) was collected and extracted with cold acetone (2 × 20 ml portions). A dark blue solid (A) (375 mg) remained undissolved; evaporation of the acetone gave a nearly colourless solid (2.21 g) which was dissolved in chloroform and shaken with aqueous 2M-sodium hydroxide (3 × 15 ml). Evaporation of the chloroform layer gave 2,3,6,7,10,11-hexamethoxytriphenylene (81 mg). Acidification of the alkaline solution precipitated a colourless solid (1.64 g) which was collected and extracted with boiling methanol (2 × 20 ml). The insoluble residue (250 mg) crystallised from chloroform-ether and sublimed at 240° and 0.001 mmHg to give 1,3-dichloro-7,8-dimethoxy-4-(3,4-dimethoxyphenyl)dibenzofuran-2-ol [IV; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (225 mg, 14%), m.p. 264–266° (decomp.) (Found: C, 58.9; H, 4.3. C<sub>22</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>6</sub> requires C, 58.8; H, 4.05%),  $\nu_{\max}$  3520 cm<sup>-1</sup> (OH),  $\lambda_{\max}$  256 (log  $\epsilon$  4.38) and 322 nm (4.42),  $\lambda_{\text{inf}}$  330 nm (4.42),  $m/e$  448 (100%, M<sup>+</sup>), 433 (4%, M - Me), 370 (8%, M - Me - COCl), and 224 (11%, M<sup>2+</sup>). Evaporation of the methanolic solution gave a solid (1.35 g) which was separated by t.l.c. on silica gel [chloroform-benzene (4 : 1, v/v)] into 2,6-dichlorohydroquinone (682 mg) and a second, more mobile, component. The latter crystallised from methanol to give 1,3-dichloro-7,8-dimethoxydibenzofuran-2-ol (IV; X = Cl, Y = H) as needles (125 mg, 6%), m.p. 200–201° (Found: C, 53.4; H, 3.2; OMe, 20.1. C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> requires C, 53.7; H, 3.2; 2 OMe, 19.8%),  $\nu_{\max}$  3500br cm<sup>-1</sup> (OH),  $\lambda_{\max}$  223 (log  $\epsilon$  4.45), 265 (4.01), 278 (3.74), and 315 nm (4.37),  $\lambda_{\text{inf}}$  243 (4.22), 322 (4.30), and 345 nm (3.43),  $\delta$  7.67, 7.42, and 7.04 (each 1H, sharp s, H-9, H-4, and H-6), 5.75br (1H, s, ArOH), and 3.98 and 3.96 (each 3H, s, ArOCH<sub>3</sub>).

A solution of the blue solid (A) in chloroform was filtered through a short column of silica gel. Elution with chloroform-benzene (4 : 1 v/v) afforded 2,3,6,7,10,11-hexamethoxytriphenylene (290 mg; total 37%). The purple zone at the top of the column was separated, shaken with aqueous 5% sodium dithionite,<sup>1</sup> and extracted repeatedly with boiling acetone. Anhydrous iron(III) chloride was added to the acetone solution and the resulting precipitate was washed with 2M-hydrochloric acid and with ethanol to give the naphthacenequinone (II) as a purple solid (72 mg, 8%), identical (i.r.) with an authentic specimen.<sup>1</sup>

(b) *Excess of veratrole*. A mixture of powdered 2,6-dichlorobenzoquinone (1.0 g, 0.006 mol), veratrole (2.0 g, 0.015 mol), and 70% v/v aqueous sulphuric acid (10 ml) was shaken for 30 min, kept at room temperature for 1 week, and diluted with water (25 ml). The resulting oily solid was collected and extracted with cold acetone (2 × 10 ml portions). A purple solid (A) (380 mg) remained undissolved; evaporation of the acetone afforded a purple semi-solid residue which was shaken with cold ether (2 × 10 ml). The insoluble residue crystallised from nitromethane-ethanol to give 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone [III; X = Cl, Y = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] (36 mg) as purple needles, m.p. 211–213° (Found: M<sup>+</sup> 448.0484. C<sub>22</sub>H<sub>18</sub><sup>35</sup>Cl<sub>2</sub>O<sub>6</sub> requires M, 448.0480),  $\nu_{\max}$  1669 and 1650 cm<sup>-1</sup> (quinone C=O),  $\lambda_{\max}$  (CHCl<sub>3</sub>) 266 (log  $\epsilon$  4.32), 284 (4.40), 338 (3.37), and 516 nm (3.61),  $m/e$  448 (100%, M<sup>+</sup>), 417 (14%, M - CH<sub>3</sub>O), 413 (19%, M - Cl), 389 (30%, M - CH<sub>3</sub>O - CO), and 385 (6%, M - Cl - CO). The ethereal solution was washed with aqueous 2M-sodium hydroxide and evaporated to give veratrole (0.32 g). The alkaline aqueous layer was acidified, extracted with ether,

and a solution of the resulting brown gum (0.83 g) in chloroform was treated with anhydrous iron(III) chloride (100 mg) and then shaken successively with 5M-hydrochloric acid and 2M-sodium hydroxide. Evaporation of the chloroform layer gave a red residue (31 mg) from which more 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (11 mg; total 4%) was obtained by t.l.c. on silica gel (chloroform). Acidification of the aqueous alkaline solution gave a brown solid (365 mg) which was separated by t.l.c. on silica gel [chloroform-benzene (4 : 1, v/v)] into 2,6-dichlorohydroquinone (295 mg) and 1,3-dichloro-7,8-dimethoxydibenzofuran-2-ol (18 mg, 2%).

Treatment of the purple solid (A) as described in (a) afforded 2,3,6,7,10,11-hexamethoxytriphenylene (297 mg, 39%) and 2,5,6,9,12,13-hexamethoxydibenzo[*fg,op*]naphthacene-1,10-quinone (35 mg, 7%).

*Arylation of Quinones by Diazotised 3,4-Dimethoxyaniline*.—(a) *2,5-Dichlorobenzoquinone*. Sodium nitrite (0.34 g) in water (4 ml) at 0° was added to a solution of 3,4-dimethoxyaniline<sup>8</sup> (0.61 g) in 2M-hydrochloric acid (10 ml) at 0°, followed by sodium acetate (1.8 g) in water (10 ml) at 0°. The solution was added during 4 min to a stirred solution of 2,5-dichloro-1,4-benzoquinone (0.78 g) in ethanol (40 ml) and acetone (50 ml) at 0°, the mixture was kept at 0° for 3 h, and the resulting red precipitate (A) (160 mg) was collected. The filtrate was diluted with water (40 ml) and kept at room temperature for 3 h, and the solid (B) (260 mg) which separated was collected. Extraction of the solid (A) with boiling methanol gave a soluble fraction (C) and an insoluble residue. The latter crystallised from chloroform-acetone to give 2,5-dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone as red rhombohedra (95 mg, 11%), m.p. 303–304°. Crystallisation of the combined fractions (B) and (C) from methanol gave 2,5-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone as red crystals (320 mg, 26%), m.p. 177–178°. The quinones were identical with the corresponding specimens prepared as described above.

(b) *2,6-Dichlorobenzoquinone*. A solution of the quinone (1.17 g) in acetone (50 ml) was treated as in (a) with the buffered solution of the diazonium salt prepared from 3,4-dimethoxyaniline (0.92 g). The mixture was filtered and the resulting dark solid was washed with ether (15 ml) and crystallised from nitromethane-ethanol to give 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone as purple needles (35 mg, 3%), identical with the specimen described above. The filtrate was diluted with water (150 ml) and shaken with ether (2 × 50 ml). All the ethereal solutions were combined, washed with 2M-sodium hydroxide, and evaporated. A solution of the red residue in benzene (5 ml) was filtered through a column of silica gel which was washed with light petroleum (b.p. 60–80°)-ether (33 : 1, v/v). Unchanged 2,6-dichlorobenzoquinone (120 mg) was eluted first, followed by 2,6-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (III; X = Cl, Y = H), which crystallised from light petroleum (b.p. 60–80°) as red prisms (260 mg, 14%), m.p. 161–163° (Found: C, 53.6; H, 3.4; Cl, 21.7. C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> requires C, 53.7; H, 3.2; Cl, 22.65%),  $\nu_{\max}$  1690 and 1650 cm<sup>-1</sup> (quinone C=O),  $\lambda_{\max}$  225 (log  $\epsilon$  4.13), 278 (4.20), and 490 nm (3.19),  $\lambda_{\text{inf}}$  267 (4.18) and 317 nm (3.24).

*Cyclisations of Aryl-1,4-benzoquinones*.—(a) *Acid-catalysed*. A mixture of powdered 2,6-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (20 mg) and 70% v/v aqueous sulphuric acid (3 ml) was shaken overnight and diluted with water (10 ml). The resulting solid was collected and

<sup>8</sup> F. Pollecoff and R. Robinson, *J. Chem. Soc.*, 1918, **113**, 645.

crystallised from aqueous methanol giving 1,3-dichloro-7,8-dimethoxydibenzofuran-2-ol as needles (14 mg), m.p. 199—201°. Similar treatment of 2,5-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (51 mg) gave 1,4-dichloro-7,8-dimethoxydibenzofuran-2-ol (45 mg), and 2,6-dichloro-3,5-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (10 mg) gave 1,3-dichloro-7,8-dimethoxy-4-(3,4-dimethoxyphenyl)dibenzofuran-2-ol (6 mg). The products were identical with the corresponding dibenzofurans described earlier. 2,5-Dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone was recovered unchanged after being shaken with 70% v/v aqueous sulphuric acid for 3 days.

(b) *Photochemical*. A solution of 2,5-dichloro-3-(3,4-dimethoxyphenyl)-1,4-benzoquinone (4 mg) in chloroform (AnalaR; 200 ml) was exposed to June sunlight (filtered through glass) for 16 days and evaporated. The residue was separated by repeated t.l.c. on silica gel (chloroform)

into starting material and 1,4-dichloro-7,8-dimethoxydibenzofuran-2-ol (2 mg), identical (u.v. and mass spectra; and t.l.c.) with an authentic specimen.

A similar reaction with 2,5-dichloro-3,6-bis-(3,4-dimethoxyphenyl)-1,4-benzoquinone (4 mg) (exposed for 5 days) gave 1,4-dichloro-7,8-dimethoxy-3-(3,4-dimethoxyphenyl)dibenzofuran-2-ol [IV; X = 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Y = Cl] (3 mg), m.p. 259—261° (Found:  $M^+$ , 448.0478. C<sub>22</sub>H<sub>18</sub><sup>35</sup>Cl<sub>2</sub>O<sub>6</sub> requires  $M$ , 448.0480),  $\lambda_{\max}$  (CHCl<sub>3</sub>) 320 nm (log  $\epsilon$  4.49),  $\lambda_{\text{inf}}$  264 (4.15) and 328 nm (4.44),  $m/e$  448 (100%,  $M^+$ ), 433 (4%,  $M - \text{Me}$ ), 370 (8%,  $M - \text{Me} - \text{COCl}$ ), and 224 (8%,  $M^{2+}$ ).

No reaction occurred in either case when similar solutions were kept for 70 days in the dark.

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