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Dibenzofurans from the Acid-catalysed Reaction of Alkyl-*p*-benzoquinones with Recorcinol

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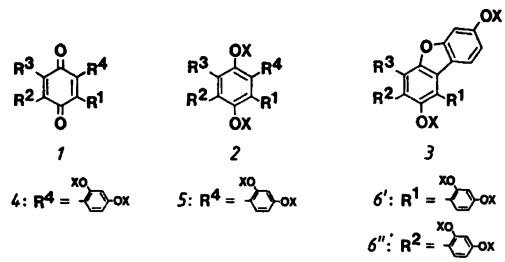
In the presence of a catalytic amount of sulfuric acid, *p*-benzoquinone and its methyl derivatives react with resorcinol in acetic acid (12 M, aq) at reflux temperature to give alkyldibenzofuran-2,7-diols with the general structure *3*, 2,4-dihydroxyphenyldibenzofurandiols with the general structure *6* and biphenyl-2,2′,4,5′-tetrols with the general structure *5*.

One of us recently described the reactions of 1,4-naphthoquinone with polyhydric phenols in acetic acid containing a trace of sulfuric acid.[1] Reaction with resorcinol, for example, gives the benzonaphthofurans *3h* and *6′h* (at 118 °C) or 2-(2,4-dihydroxyphenyl)-1,4-naphthoquinone (*4h*) (at 20 °C). The closely analogous acid-catalysed oligomerisation of various *p*-benzoquinones and 1,4-naphthoquinone also furnishes furanoid products in good yields.[2-6]

Benzoquinone and resorcinol in aqueous sulfuric acid yield a black product which after reduction and methylation affords the permethyl ether of the biphenyltetrol *5a* and a hexamethoxy-*m*-terphenyl along with polymers.[7] Benzoquinone and pyrogallol react similarly.[8] Furanoid products have not been isolated from these reactions. We have now studied the reactions of *p*-benzoquinone and its methyl derivatives with resorcinol and have found that, under certain conditions, dibenzofurans were formed, in some cases in good yields.

Each of the quinones was condensed with an equimolar amount of resorcinol in refluxing acetic acid (12 M, aq) containing a trace of sulfuric acid. This afforded a mixture of phenolic products, which on methylation followed by chromatography furnished the permethyl ethers of a dibenzofurandiol, a dihydroxyphenyldibenzofurandiol and a biphenyltetrol with the general structures *3*, *6* and *5*, respectively. The products and yields obtained from each of the quinones are listed in Table 1.



Scheme 1. *a*–*h*: X = H; a_M–h_M: X = Me. The following applies except when otherwise stated (see formulae *3*–*8*).

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	H	H
c	H	H	Me	H
d	H	Me	Me	H
e	Me	H	Me	H
f	Me	Me	H	H
g	Me	Me	Me	H
h	H	CH=CH–CH=CH		H

The reactions of one of the quinones were studied more closely. 2,3-Dimethylquinone (*1d*) (2 mol) and resorcinol (1 mol), upon treatment with a trace of sulfuric acid in acetic acid and water at room temperature, gave the ruby red dihydroxyphenylquinone *4d*. Reduction and subsequent methylation yielded the permethyl ether of the biphenyltetrol *5d*. This compound was also prepared starting from

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Table 1. Title reaction products and isolated yields of their permethyl ethers.

Quinone	Product (Yield, %)			
Unsubstituted (1a)	*3a*(1) [a]	*5a*(26) [a]		*2a*(45) [a]
Methyl (*1b*=*1c*)	*3b*(4)	*5b*(15)	*6′,6″,b,c*(15)	*2b*(12)
	3c(5)	*5c*(10)		
2,3-Dimethyl (*1d*)	*3c*(25)	*5d*(25)	*6′d*(8)	*2d*(10)
2,5-Dimethyl (*1e*)	*3e*(34)	*5e*(3)	*6″e*(11)	*2e*(12)
2,6-Dimethyl (*1f*)	*3f*(57)			*2f*(5)
Trimethyl (*1g*)	*3g*(75) [b]			
Naphtho (*1h*)	*3h*(65) [c]		*6′h*(15–20) [c]	

[a] GC yields. [b] Isolated as the phenol. [c] Isolated as the peracetates.

2,3-dimethylquinone and diazotised 2,4-dimethoxyaniline.

When treated with a trace of sulfuric acid in refluxing acetic acid the biphenyltetrol *5d* was recovered almost quantitatively. However, when refluxed with concentrated hydrobromic acid the same compound gave the dibenzofurandiol *3d* (85 %).

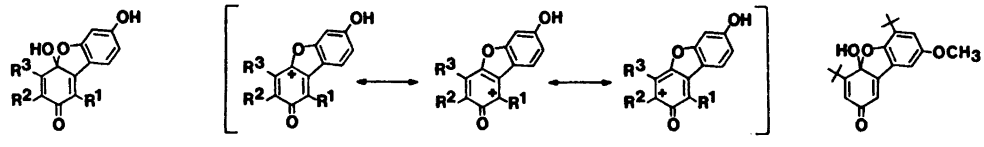
The dihydroxyphenylquinone *4d* reacted with resorcinol in acid solution furnishing the dihydroxyphenyldibenzofurandiol *6′d* (30 %).

The structural assignments of all new compounds were based on their spectral properties (see Experimental part) and their mode of formation.

The mechanism of the above-mentioned quinone phenol condensations should be similar to that recently proposed to account for the formation of dibenzofurans in the quinone oligomerisation reactions.[6] Thus a quinone reacts with resorcinol to give a biphenyltetrol *5*, which does not undergo direct dehydration to a dibenzofurandiol (*cf.* above and Ref. 4). Instead it is oxidized by the starting quinone to afford a dihydroxyphenylquinone *4*. This undergoes isomerisation to a hemiketal *7*, which, on protonation, loses water furnishing a phenoxenium ion *8*. Reduction of this gives a dibenzofuran *3* while the starting quinone is regenerated. Alternatively, the phenoxenium ion reacts with resorcinol to give a dihydroxyphenyldibenzofuran of type *6′* or *6″*. We have recently found some experimental evidence for this mechanism.[9]

Whereas benzoquinone gave only a trace of a dibenzofurandiol of type *3*, better results were obtained with more substituted quinones. Thus, 2,6-dimethyl- and trimethylquinone (*1f* and *1g*) both gave good yields of the dibenzofurandiols *3f* and *3g*, respectively. However, 2,3-dimethyl- and 2,5-dimethylquinone (*1d* and *1e*) both gave lower yields of the dibenzofurandiols *3d* and *3e*. The ionic intermediates, *8f* and *8g*, from the former two quinones both possess two reactive positions which, however, are blocked by methyl groups. Hence further attack of resorcinol is precluded and the reaction is forced to proceed *via* the alternative route, *i.e.* reduction to the dibenzofurandiols *3f* and *3g*. The ionic intermediates, *8d* and *8e*, from the latter two quinones, however, are free to undergo attack by resorcinol and this reaction competes with reduction.

It is known that, in some cases, 2-methylquinone undergoes addition to give a mixture of 5- and 6-substituted methylhydroquinone derivatives.[10] Similarly, this quinone and resorcinol furnished the two dibenzofurandiols



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3b and *3c* in a 6:7 ratio and the two methylbiphenyltetrols *5b* and *5c* in a 3:2 ratio. Obviously the 6-methylated intermediate, arylquinone *4c*, must undergo ring-closure more rapidly than the 5-methylated intermediate *4b*. In this connection it may be noted that the sterically crowded stable hemiketal *9* [11] cannot be isolated in its isomeric 6-*t*-butyl-2-(hydroxyaryl)quinone form. The hemiketal *9* readily yields dibenzofurans on acid-catalysed reduction or on reaction with resorcinol.[9]

The approach to dibenzofurans discussed here has recently been used by one of us in the first step in the synthesis of a natural product, ruscodibenzofuran (8-acetyl-1,4-dimethyl-7-hydroxydibenzofuran).[12]

EXPERIMENTAL

General

Melting points are uncorrected and were determined using capillary tubes in a silicon oil bath (those of the phenols *3d-g* and compounds *4d*, *5d* and *6'd* using sealed evacuated capillary tubes). Ultraviolet spectra: solvent, ethanol; data representation, λ_{max} (log ε). ^{1}H NMR: 60 MHz; solvent, chloroform *d*: internal standard, TMS; primed position numbers refer to 2,4-dimethoxy- or 2,4-dihydroxyphenyl group. The ^{1}H NMR spectra of compounds $3a_M - g_M$ are listed in Table 2. MS: Ionisation potential 70 eV; data representation, *m/e* (relative intensity). Derivatives were prepared as follows: Permethyl ethers were obtained by reacting the phenols in methanol under nitrogen with an excess of dimethyl sulfate using an excess aqueous sodium hydroxide as base; acetates were prepared from phenols by briefly refluxing these in acetic anhydride containing a trace of pyridine and similarly from quinones in the presence of zinc dust; dibenzofurandiols were in some cases prepared from the corresponding dimethyl ethers by refluxing these for 12 h with concentrated hydrobromic acid.

Title reaction procedure. Unless otherwise stated the quinone (10 mmol) and resorcinol (10 mmol) were refluxed in dilute acetic acid (70 % v/v, aq, 10 ml). When sulfuric acid (50 % v/v, aq, 1 ml) was added an exothermic reaction started, giving a brown red solution, the colour of which then slowly faded. The course of the reaction was followed by TLC (silica gel, precoated aluminium plates, ether, samples were shaken with saturated sodium hydrogen carbonate solution and ether before application to the plate). When no further change was observed (in all cases within 2 h) the reaction mixture was cooled and sodium carbonate (1.2 g) was added to neutralize the sulfuric acid. The acetic acid was evaporated and the residue was dissolved in methanol (50 ml) and the inorganic salts were removed by filtration. The filtrate was evaporated to dryness and methylated. The product was steam distilled to remove resorcinol dimethyl ether and the hydroquinone dimethyl ether (yields, see Table 1, identified by its m.p. or ^{1}H NMR). The residue was chromatographed (silica gel, 70 – 200 mesh, 100 g, CH_2Cl_2 as eluent) to give a dibenzofuran fraction followed by a fraction containing a mixture of the tetramethyl ethers of compounds of types *5* and *6*. This mixture was further separated by repeated column chromatography (silica gel, finer than 230 mesh, CH_2Cl_2 as eluent) and/or fractional vacuum distillation.

Benzoquinone resorcinol reaction

The crude methylated product contained two major products on analysis by gas chromatography (SE30, 140 – 160 °C), 1,4-dimethoxybenzene ($1a_M$) (45 %) and 2,2',4,5'-tetramethoxybiphenyl ($5a_M$) (26 %). 2,7-Dimethoxydibenzofuran ($3a_M$) was present in a very low yield (approximately 1 %). The amounts of the identified compounds were all calculated using 1,4-dimethoxynaphthalene as an internal standard. A kugelrohr distillation (80 – 140 °C/0.1 mmHg) gave two volatile fractions: 1,4-dimethoxybenzene (0.64 g, 46 %) and 2,2',4,5'-tetramethoxybiphenyl ($5a_M$) (0.54 g, 20 %), m.p. 103 – 104 °C (ethanol) (Lit.[7] 104.5 – 106.0 °C). When refluxed with concentrated hydrobromic acid for 12 h under nitrogen the latter compound gave after methylation 2,7-dimethoxydibenzofuran ($3a_M$); m.p. 112 – 113 °C (ethanol) (Lit.[13] 112 – 113 °C).

Methylquinone resorcinol reaction

The dibenzofuran fraction (0.22 g, 9 %) was a 6:7 mixture (by NMR) of the 3- and 4-methyldibenzofurans, which were separated by repeated chromatography (silica gel, finer than 230 mesh, CH_2Cl_2 as eluent) to give:

2,7-Dimethoxy-3-methyldibenzofuran ($3b_M$). Needles (ethanol), m.p. 101.0 – 101.5 °C. Anal. $C_{15}H_{14}O_3$: C, H. ^{1}H NMR: see Table 2.

2,7-Dimethoxy-4-methyldibenzofuran ($3c_M$). Prisms (ethanol), m.p. 84.0 – 84.5 °C. Anal. $C_{15}H_{14}O_3$: C, H. ^{1}H NMR: see Table 2.

The tetramethyl ether fraction gave:

2,7-Dimethoxy-X-(2,4-dimethoxyphenyl)-Y-methyldibenzofurans. The residue from a fractional vacuum distillation of the tetramethyl ether fraction was rechromatographed to give an inseparable mixture of resorcyldibenzofuran ethers (0.57 g, 15 %). MS: 378(100, *M*), 363(15),

348(14), 332(17), 317(8), 179(15). ^{1}H NMR: δ 2.2–2.7 (3 H, m, ArCH_3), 3.4–4.0 (12 H, m, 4 OCH_3) and 6.4–7.4 (7 H, m, 7 ArH).

The volatile component of the tetramethyl ether fraction (0.61 g, 25 %) was a mixture of the tetramethyl ethers of the 4-methylbiphenyl *5b* and the 3-methylbiphenyl *5c*. When refluxed with concentrated hydrobromic acid this mixture gave, after methylation, a 3:2 mixture (by ^{1}H NMR) of 2,7-dimethoxy-3-methyldibenzofuran (*3b*$_M$) and 2,7-dimethoxy-4-methyldibenzofuran (*3c*$_M$). Column chromatography of the biphenyl mixture (0.50 g) gave:

4-Methyl-2,2',4',5-tetramethoxybiphenyl (5b$_M$*).* (0.26 g). Prisms (ethanol), m.p. 117.0–117.5 °C. Anal. $C_{17}H_{20}O_4$: C, H. ^{1}H NMR: δ 2.24 (3 H, s, ArCH_3), 3.68, 3.74, 3.76, 3.82 (12 H, 4 s, 4 OCH_3), 6.47, (1 H, dd, J 2.5 and 8.4 Hz, $H_{5'}$) 6.52 (1 H, d, J 2.5 Hz, $H_{3'}$), 6.70 and 6.72 (2 H, 2 s, H_3, and H_6), 7.15 (1 H, d, J 8.4 Hz, $H_{6'}$).

3-Methyl-2,2',4',5-tetramethoxybiphenyl (5c$_M$*).* (0.18). Vacuum distillation (*ca* 110 °C/0.2 mmHg) gave a viscous, colourless oil which could not be crystallized. Anal $C_{17}H_{20}O_3$: C, H. MS: 288(100, *M*), 273(70), 259(33), 243(22), and 228(10). ^{1}H NMR: δ 2.27 (3 H, s, ArCH_3), 3.31, 3.70, 3.71, and 3.78 (12 H, 4 s, 4 OCH_3), 6.47 (1 H, dd, J 2.5 and 8.4 Hz, $H_{5'}$), 6.52 (1 H, d, J 2.5 Hz, $H_{3'}$), 6.68 (2 H, broad s, H_4 and H_6), 7.15 (1 H, d, J 8.4 Hz, $H_{6'}$).

2,3-Dimethylquinone resorcinol reaction

An experiment performed according to the title reaction procedure resulted in the products and yields presented in Table 1. These products were also obtained in the following way:

*6-(2,4-Dihydroxyphenyl)-2,3-dimethylbenzoquinone (*4d*).* Solutions of 2,3-dimethylquinone (*1d*) (2.00 g, 14.7 mmol) in acetic acid (5 ml) and resorcinol (1.05 g, 9.5 mmol) in water (10 ml) were mixed and sulfuric acid (50 % v/v, aq, 1 ml) was added. On scratching or seeding, the product started to separate and was collected after 1 h. Recrystallization from dilute acetic acid gave long red needles (2.1 g, 60 %), m.p. 180 °C (dec.). Found: C 68.1; H 4.8. Calc. for $C_{14}H_{12}O_4$: C 68.8; H 4.9 MS: 244(100, *M*), 229(10), 227(8), 216(22), 201(7), 187(10). 173(13), 161(13), 134(15) and 110(6). IR (KBr): 1600 (s, conjugated *C*=*O*), and 3500 (broad, H-bonded *OH*) cm^{-1}. UV: 246(4.23), 278(3.89), 318(3.48), 450(3.35) nm; upon addition of a few drops of saturated sodium carbonate solution, the maximum at 450 nm was shifted to 575(3.45) nm (*cf.* Refs. 1 and 14). ^{1}H NMR (methanol-d_4): δ 2.10 (6 H, s, 2 ArCH_3), 4.90 (2 H, broad s, 2 O*H*), 6.37 (1 H, d, J 2.4 Hz, $H_{3'}$), 6.38 (1 H, dd, J 2.4 and 9.2 Hz, $H_{5'}$), 6.76 (1 H, s, H_5), 6.97 (1 H, d, J 9.2 Hz, $H_{6'}$).

*3,4-Dimethylbiphenyl-2,2',4',5-tetrol (*5d*).* The quinone *4d* in ether was shaken with an aqueous solution of sodium dithionite until the ether phase was colourless. After washing with brine, drying (Na_2SO_4) and evaporating, the product was obtained as an almost colourless powder. Yield 98 %. Sublimed material had m.p. 202–204 °C. Found: C 67.8; H 5.3. Calc. for $C_{14}H_{14}O_4$: C 68.3; H 5.9.

When this biphenyltetrol was refluxed under N_2(4 h) in an oxygen-free solution of acetic acid (70 % v/v, aq) containing sulfuric acid (6 % v/v) and a trace of zinc dust, the starting material was recovered as its tetramethyl ether after methylation in 98 % yield (by GLC, SE30 250°). The dibenzofuran *3d*$_M$ was formed in less than 2 % yield.

Tetraacetate: M.p. 131–132 °C (ethanol). Anal. $C_{22}H_{22}O_8$: C, H. UV: 220(4.69), 236(4.51), 291(3.11), 300(3.05) nm (all were inflexion points.)

Tetramethyl ether: M.p. 101–103 °C (ethanol). Anal. $C_{18}H_{12}O_4$: C, H. ^{1}H NMR: δ 2.17, 2.22 (6 H, 2 s, 2 ArCH_3), 3.32, 3.74, 3.76, 3.80 (12 H, 4 s, 4 OCH_3), 6.52, 6.59 (2 H, 2 m, $H_{5'}$ and $H_{3'}$), 6.64 (1 H, s, H_5), 7.22 (1 H, d, J 8.3 Hz, $H_{6'}$). This compound was also prepared using the method of Brassard and l'Ecuyer.[15] 2,4-Dimethoxyaniline was diazotized and treated with 2,3-dimethylquinone to give 6-(2,4-dimethoxyphenyl)-2,3-dimethylquinone (*4d*$_M$), which was reduced with sodium dithionite. The resulting hydroquinone was methylated to give a compound identical with the methyl ether of *5d*.

*3,4-Dimethyldibenzofuran-2,7-diol (*3d*).* 3,4-Dimethylbiphenyl-2,2',4',5-tetrol (*5d*) (0.9 g) was refluxed with hydrobromic acid (48 %, 25 ml) under nitrogen for 24 h. After cooling, the product was collected by filtration and washed with water and dried. Yield 0.7 g (85 %). M.p. 248–249 °C (sublimed material). Anal. $C_{14}H_{12}O_3$: C, H.

Diacetate: M.p. 159–161 °C (ethanol). Anal. $C_{18}H_{16}O_5$: C, H. UV: 220(4.50), 244(4.15), 253(4.22), 291(4.28), 300(4.21), 330(2.86) nm.

Dimethyl ether: M.p. 115–117 °C (ethanol). Anal. $C_{16}H_{16}O_3$: C, H. ^{1}H NMR: see Table 2.

*1-(2,4-Dihydroxyphenyl)-3,4-dimethyldibenzofuran-2,7-diol (*6'd*).* The quinone *4d* (1 g, 4 mmol) in acetic acid (15 ml) was mixed with resorcinol (5 g, 45 mmol) in aqueous sulfuric acid (25 % v/v, 20 ml) and the mixture was stirred overnight. The crystals, which separated, were collected and purified by sublimation. Yield 0.38 g (30 %), m.p. 240 °C (dec.). Anal $C_{20}H_{16}O_5$: C, H.

Tetraacetate: M.p. 192–194 °C (ethanol). Anal. $C_{28}H_{24}O_9$: C, H. UV: 220(4.61), 254(4.18), 292(4.25), and 300(4.21) nm.

Tetramethyl ether: M.p. 141–142 °C (ethanol). Found: C 73.0; H 6.1. Calc. for $C_{24}H_{24}O_5$: C 73.5; H 6.1.^{1}H NMR: δ 2.37 and 2.48 (6 H, 2 s, 2 ArCH_3), 3.46, 3.62, 3.74 and 3.84 (12 H, 4 s, 4 OCH_3), and 6.50–7.40 (6 H, several m, 6 ArH).

Table 2. 60 MHz ^{1}H NMR spectral data for dibenzofurans $1a_M - 1g_M$ in $CDCl_3$.

H/Me	$3a_M$	$3b_M$ [a]	$3c_M$ [b]	$3d_M$	$3e_M$ [c]	$3f_M$	$3g_M$
Chemical shifts (δ)							
1 – H/Me	7.30(dd)	7.24(s)	7.14(d)	7.20(s)	2.52(s)	2.58(s)	2.52(s)
3 – H/Me	6.94(dd)	2.30(bs)	6.78(bd)	2.25(s)	6.86(bs)	2.38(s)	2.26(s)
4 – H/Me	7.41(dd)	7.32(bs)	2.50(bs)	2.47(s)	2.46(bs)	7.15(s)	2.38(s)
6 – H	7.02(dd)	7.06(dd)	7.07(dd)	7.05(dd)	7.08(dd)	7.05(d)	7.08(d)
8 – H	6.92(dd)	6.93(dd)	6.90(dd)	6.90(dd)	6.90(dd)	6.90(dd)	6.90(dd)
9 – H	7.75(dd)	7.75(dd)	7.73(dd)	7.77(dd)	7.87(dd)	7.82(d)	7.80(d)
OMe	3.80(s)	3.80(s)	3.82(s)	3.81(s)	3.80(s)	3.69(s)	3.68(s)
OMe	3.82(s)	3.85(s)	3.82(s)	3.85(s)	3.80(s)	3.80(s)	3.78(s)
Coupling constants J(H,H) (Hz)							
1,3	2.4		2.4				
1,4	0.6	0					
3,4	9.0						
6,8	2.2	2.3	2.2	2.3	2.3	2.3	2.2
6,9	0.6	0.6	0·6	0.5	0.6	0	0
8,9	8.5	8.3	8.4	8.3	8.5	8.5	8.5

[a] Irradiation at δ 2.30 gave a sharp singlet at δ 7.32. [b] Irr. at δ 2.50 gave a sharp doublet at δ 6.78. [c] Irr. at δ 2.46 gave a sharp singlet at δ 6.86.

2,5-Dimethylquinone resorcinol reaction

2,7-Dimethoxy-1,4-dimethyldibenzofuran ($3e_M$). (34 %) Needles (ethanol), m.p. 100 – 101 °C. Anal. $C_{16}H_{16}O_3$: C, H. ^{1}H NMR: see Table 2. Phenol: M.p. 208 – 211 °C. Anal. $C_{14}H_{12}O_3$: C, H. Diacetate: M.p. 137 – 138 °C. Anal. $C_{18}H_{16}O_5$: C, H. UV: 225(4.57), 247(4.09), 256(4.19), 284(4.27), 296(sh, 3.93), 306(sh, 3.64) nm.

2,7-Dimethoxy-3-(2,4-dimethoxyphenyl)-1,4-dimethyldibenzofuran ($6''e_M$). (11 %). M.p. 140 – 141 °C. Anal. $C_{24}H_{24}O_5$: C, H. ^{1}H NMR: δ 2.20, 2.65 (6 H, 2 s, 2 ArCH_3), 3.41, 3.75, 3.86, 3.87 (12 H, 4 s, 4 OCH_3), 6.50 (1 H, dd, J 2.7 and 8.3 Hz, $H_{5'}$), 6.61 (1 H, d, J 2.7 Hz, $H_{3'}$), 6.86 (1 H, dd, J 2.4 and 8.8 Hz, H_8), 7.05 (1 H, d, J 2.4 Hz, H_6), 7.08 (1 H, d, J 8.3 Hz, $H_{6'}$), 7.84 (1 H, d, J 8.8 Hz, H_9).

2,5-Dimethyl-2',3,4',6-tetramethoxybiphenyl ($5e_M$), (approx. 3 %) was not isolated pure and was only characterized by its MS: 302 [100 %, M ($C_{18}H_{12}O_4$ requires M = 302)].

2,6-Dimethylquinone resorcinol reaction

2,7-Dimethoxy-1,3-dimethyldibenzofuran ($3f_M$) (57 %). M.p. 63 – 64 °C (ethanol). Anal. $C_{16}H_{16}O_3$: C, H. ^{1}H NMR: see Table 2. Phenol: M.p. 234 – 237 °C. Anal. $C_{14}H_{12}O_3$: C, H: Diacetate: M.p. 165.0 – 165.5 °C. Anal. $C_{18}H_{16}O_5$, C, H. UV: 223(4.60), 247(4.12), 254(4.26). 287(4.34), 298(sh, 4.16) nm.

Trimethylquinone resorcinol reaction

1,3,4-Trimethyldibenzofuran-2,7-diol (3g). A mixture of trimethyl-*p*-quinone (1.67 g, 11 mmol) and resorcinol (1.40 g, 13 mmol) in 60 % acetic acid (25 ml) and sulfuric acid (5 ml) was refluxed overnight. After dilution with hot water (100 ml) the mixture was cooled and the brown precipitate collected by filtration and dried (2.40 g). NMR showed that the product was essentially pure. Vacuum sublimation (190 °C 0.1 mmHg) gave colourless needles. Yield 1.92 g (75 %), m.p. 198 – 200 °C (dec.). Anal. $C_{15}H_{14}O_3$: C, H.

Diacetate: Needles (ethanol), m.p. 185 °C. Anal. $C_{19}H_{18}O_5$: C, H. UV: 224(4.61), 247(4.15), 256(4.26), 286(4.35), 297(sh, 4.12) nm.

Dimethyl ether: Plates (ethanol), m.p. 121 – 122 °C. Anal. $C_{17}H_{18}O_3$: C, H. ^{1}H NMR: see Table 2.

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