Benzoquinones and Related Compounds. Part 6.[1] Addition of Benzenesulfinic Acid to Substituted 1,4-Quinones

J. Malcolm Bruce* and Paul Lloyd-Williams
Department of Chemistry, The University, Manchester M13 9PL, UK

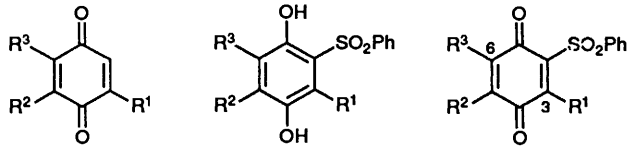
Benzenesulfinic acid adds to 1,4-quinones in the presence of trifluoroacetic acid affording phenylsulfonylhydroquinones. Addition occurs predominantly at the 6-position for methyl-, *tert*-butyl- and trifluoromethyl-1,4-benzoquinone, but at the 5-position for methoxy-1,4-benzoquinone. Addition to acyl-1,4-benzoquinones occurs exclusively at the 3-position, but under similar conditions phenylsulfonyl-1,4-benzoquinone affords a mixture of 2,3- and 2,6-bisphenylsulfonylhydroquinones, although the former becomes the sole product in the presence of an excess of trifluoroacetic acid. These results are rationalised in terms of selective protonation of the quinone.

Oxidation of the phenylsulfonylhydroquinones yields the corresponding quinones which with 1,3-dienes give the expected Diels–Alder adducts.

The addition of benzenesulfinic acid to 1,4-benzoquinone to yield phenylsulfonylhydroquinone is one of the earliest reported instances of the addition of a sulfur nucleophile to a quinone.[2] We now report on new aspects of reactions involving the addition of benzenesulfinic acid to quinones and of reactions of the quinones derived from the products.

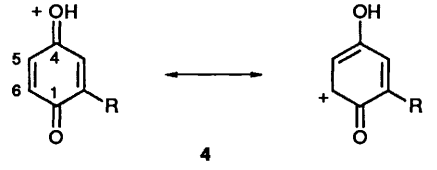
Additions of phenylsulfinate to the quinones were effected using a two-phase dichloromethane–water system with the organic phase containing sufficient trifluoroacetic acid to ensure acidity throughout the course of the reaction. The results are summarised in Table 1.

1,4-Benzoquinone and its di- and tri-methyl homologues, and 1,4-naphthoquinone and 1,4-anthraquinone afforded single, effectively Michael, addition products in good yield (Table 1, entries 1–7).



1 **2** **3**

For toluquinone (2-methyl-1,4-benzoquinone), addition occurs at both the 6- and 5-positions, with the former predominating by 3:1 (Table 1, entry 9). Since nucleophilic attack on the free quinone would be expected to occur mainly at the 5-position,[3] this result can be rationalised by invoking attack of the sulfinic acid on the protonated quinone;[4] for steric reasons protonation would be expected to occur predominantly at the 4-carbonyl group [**4** (R = Me)]. A similar argument can be



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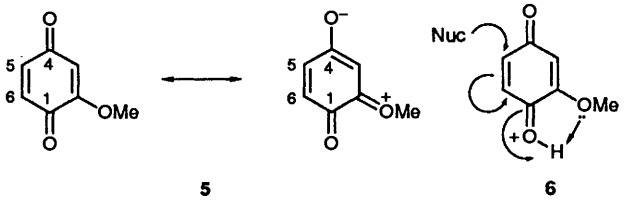
applied to *tert*-butyl-1,4-benzoquinone, for which the increased (12:1) proportion of 6-substituted product (Table 1, entry 10) arises from steric retardation of competing protonation of the 1-carbonyl group [*cf.* **4** (R = Bu^t)]. The ratio (4:1) of products from trifluoromethyl-1,4-benzoquinone (Table 1, entry 11) parallels that from toluquinone, implying a similar distribution of protonated forms, and an essentially steric effect for the inductively electron-accepting trifluoromethyl group.

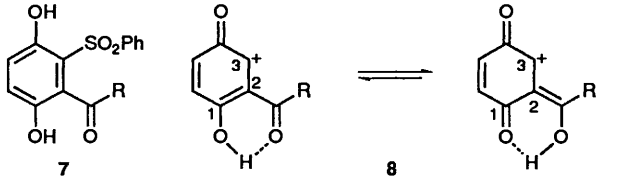
For methoxy-1,4-benzoquinone, the regioselectivity of addition is reversed, with attack occurring predominantly (9:1) at the 5-position (Table 1, entry 12). The methoxy and 4-carbonyl groups here constitute a vinylogous ester, in effect leaving the remaining enone moiety **5** to control the regiochemistry of the Michael addition, an effect which will be enhanced by the preferential protonation of the 1-carbonyl group consequent upon the presence of the adjacent methoxy group **6** as observed for some Lewis acid catalysed Diels–Alder reactions



5 **6**

of methoxy-1,4-benzoquinones.[5,6] That addition does not occur exclusively at the 5-position may be a consequence of the competing protonation of the 4-carbonyl group **4** (R = OMe) leading to activation of the 6-position.

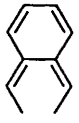
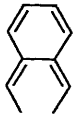
The four acyl-1,4-benzoquinones **1** (R^1 = COMe, COPh, COBu^t or CO_2Me; R^2 = R^3 = H) add benzenesulfinic acid regiospecifically (Table 1, entries 13–16) giving the corresponding 2-acyl-3-phenylsulfonylhydroquinones **7** (R = Me, Ph, Bu^t or OMe, respectively), in agreement with well-precedented[7,8] susceptibility of acyl-1,4-benzoquinones to undergo nucleophilic addition at the 3-position, control being dominated by the additional stabilisation of the intermediate due to the acyl group. However, under the conditions employed for the



7 **8**

present work, protonation of the quinone may be the dominating factor. It would be expected to occur predominantly at the 1-carbonyl group because this can lead to internally hydrogen-

Table 1 Hydroquinones from addition of benzenesulfinic acid to 1,4-quinones (quinone: $PhSO_2Na$: CF_3CO_2H = 1.0:1.1:1.1)

Entry	Quinone				Hydroquinone **2**			
		R^1	R^2	R^3	R^1	R^2	R^3	Yield (%)[a]
1	**1**	H	H	H	H	H	H	95
2	**1**	H	Me	Me	H	Me	Me	78
3	**1**	Me	Me	H	H	Me	Me	84
4	**1**	Me	H	Me	Me	H	Me	79
5	**1**	Me	Me	Me	Me	Me	Me	82
6	**1**	H			H			68
7	**1**	H			H			57
8	**1**	Me			Me			0
9	**1**	H	Me	H	H	Me	H	25[b]
					H	H	Me	75[b]
10	**1**	H	Bu^t	H	H	Bu^t	H	7[b]
					H	H	Bu^t	93[b]
11	**1**	H	CF_3	H	H	CF_3	H	20[b]
					H	H	CF_3	80[b]
12	**1**	OMe	H	H	H	OMe	H	80[b]
					H	H	OMe	20[b]
13	**1**	MeCO	H	H	MeCO	H	H	68
14	**1**	PhCO	H	H	PhCO	H	H	85
15	**1**	Bu^{t}CO	H	H	Bu^{t}CO	H	H	66
16	**1**	CO_2Me	H	H	CO_2Me	H	H	84
17	**3**	H	H	H	$PhSO_2$	H	H	46[c]
					H	H	$PhSO_2$	48
18	**3**	H	Me	Me	$PhSO_2$	Me	Me	67
19	**3**	Me	Me	H	Me	Me	$PhSO_2$	85
20	**3**	Me	H	Me	Me	$PhSO_2$	Me	92

[a] Yield of product isolated. [b] Calculated from the ratio of isomers in the total reaction product determined by ^1H NMR spectroscopy. [c] This isomer was formed exclusively, in 67% isolated yield, when the ratio of reactants was 1.0:1.1:3.8.

bonded quasi-aromatic systems such as **8**, and thus lead to exclusive addition of the nucleophile to the 3-position.

For phenylsulfonyl-1,4-benzoquinone **3** ($R^1 = R^2 = R^3 =$ H) the regiochemistry of addition is controlled by the amount of trifluoroacetic acid present (Table 1, entry 17). With 1.1 mol of acid, addition is divided almost equally between the 3- and 6-positions. On electronic grounds, attack at the 3-position would be expected to predominate, giving the intermediate **9** from which the product **2** ($R^1 = SO_2Ph$, $R^2 = R^3 =$ H) is formed by enolisation. However this enolisation places two bulky substituents *ortho* to each other, and may be sufficiently slow to permit reversal[9,10] at the intermediate, **9**, stage, regenerating the starting materials and therefore allowing the alternative mode of addition, involving protonation at the 4-carbonyl group, to compete, thus affording the 2,6-bisphenylsulfonylhydroquinone **2** ($R^1 = R^2 =$ H, $R^3 = SO_2Ph$). With 3.8 mol of trifluoroacetic acid, 2,3-bisphenylsulfonylhydroquinone was formed exclusively suggesting either (or both) enhanced protonation of the 1-carbonyl group of the quinone or catalysis of enolisation of the intermediate ketonic adduct **9**.

No such complications arise for the three isomeric dimethyl homologues of phenylsulfonyl-1,4-benzoquinone, each of which yields the corresponding bisphenylsulfonylhydroquinone (Table 1, entries 18–20).

2-Methyl-1,4-naphthoquinone failed to yield a phenylsulfonylhydroquinone. Elimination from an initial adduct such as **10** may be favoured over enolisation, since keto–enol tautomerism is much more facile[11] in 1,4-dihydroxynaphthalene than it is in 1,4-dihydroxybenzene, and the keto form is expected to be favoured by the reduction in steric repulsion between the 2- and 3-substituents,[12,13] although at 200 °C 2,3-dimethyl-1,4-naphthohydroquinone is favoured over its ketonic tautomer;[14] this effect is absent in the adduct from 1,4-naphthoquinone (Table 1, entry 6).

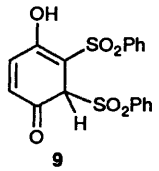
The hydroquinones corresponding to entries 1–6 in Table 1 were readily oxidised to the quinones by treatment with silver(I) oxide; oxidation of the bisphenylsulfonylhydroquinones (Table 1, entries 17–20) required phenyliodine(III) bistrifluoroacetate. Treatment of 2-phenylsulfonyl-1,4-anthrahydroquinone (Table 1, entry 7) with silver(I) oxide did not proceed cleanly, and afforded some 1,4-anthraquinone, possibly *via* base-induced elimination of phenylsulfinate from the diketonic tautomer (*cf.* ref. 15).

Addition of cyclopentadiene, 1,3-butadiene and (*E*)-penta-1,3-diene to phenylsulfonyl-1,4-benzoquinone afforded the expected Diels–Alder *endo*-adducts **11** (R = H) and **12** (R = H or Me), respectively,* that with (*E*)-penta-1,3-diene being formed regiospecifically (^1H NMR spectrum of total product) in accord with the electron accepting nature of the phenylsulfonyl group.[16]

* The products were racemic; only one enantiomer is shown.

Table 2 First ($E_{\frac{1}{2}}^1$, $Q/Q^{\bullet -}$) and second ($E_{\frac{1}{2}}^2$, $Q^{\bullet -}/Q^{2-}$) half-wave reduction potentials of quinones in dimethylformamide *vs.* saturated calomel electrode

Entry	Quinone	R^1	R^2	R^3	$E_{\frac{1}{2}}^1$/mV	$E_{\frac{1}{2}}^2$/mV
1	**1**	H	H	H	−401	−1155
2	**3**	H	H	H	−40	—
3	**1**	H	Me	Me	−543	−1269
4	**3**	H	Me	Me	−147	−1026
5	**1**	Me	Me	Me	−632	−1393
6	**3**	Me	Me	Me	−318	−1037
7	**1**	MeCO	H	H	−178	—
8	**3**	MeCO	H	H	+50	−744
9	**1**	PhCO	H	H	−211	−1048
10	**3**	PhCO	H	H	+58	−727
11	**1**	Bu^{t}CO	H	H	−286	−1116
12	**3**	Bu^{t}CO	H	H	+41	−752
13	**1**	CO_2Me	H	H	−196	−1044
14	**3**	CO_2Me	H	H	+100	−747
15	**3**	H	H	$PhSO_2$	+248	—
16	**1**	Me	H	Me	−551	−1299
17	**3**	Me	$PhSO_2$	Me	+4	—
18	**1**	Me	Me	H	−547	−1257
19	**3**	Me	Me	$PhSO_2$	−17	−802
20	**1**	H			−581	−1310
21	**3**	H			−167	−940



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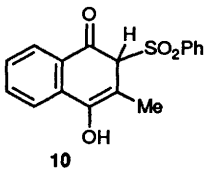

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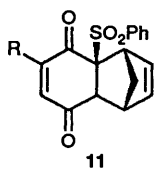

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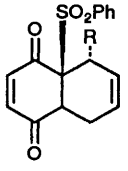

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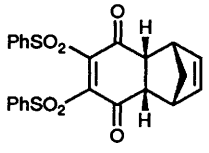

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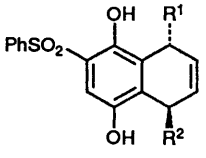

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Addition of cyclopentadiene to 2,3-bisphenylsulfonyl-1,4-benzoquinone appeared to be governed by steric factors, and afforded the adduct **13** exclusively,* thus establishing the relative orientation of the phenylsulfonyl groups in the original hydroquinone. 2,6-Bisphenylsulfonyl-1,4-benzoquinone afforded the adduct **11** (R = SO_2Ph),* the orientation of the substituents in the quinone having already been confirmed by the presence of two distinct carbonyl carbon resonances in its ^{13}C NMR spectrum.

Treatment of the buta-1,3-diene adduct **12** (R = H) with pyridine at room temperature afforded the isomer **14** (R^1 = R^2 = H) rapidly and in high yield, probably *via* an elimination–addition mechanism,[17] since the corresponding reaction with the penta-1,3-diene adduct **12** (R = Me) afforded an almost 1:1 mixture of the isomeric rearrangement products **14** (R^1 = Me, R^2 = H) and **14** (R^1 = H, R^2 = Me).*

The results of cyclic voltammetry for phenylsulfonylquinones **3** are presented in Table 2, together with data for their precursor quinones **1**.

The first half-wave reduction potential of phenylsulfonyl-1,4-benzoquinone (entry 2) is 361 mV higher than that of 1,4-benzoquinone (entry 1), whilst that of 2,3-dimethyl-5-phenylsulfonyl-1,4-benzoquinone (entry 4) and 2-phenylsulfonyl-1,4-naphthoquinone (entry 21) are 396 and 414 mV higher than those of their parents (entries 3 and 20 respectively). The increment is lowered, but only to 314 mV, by the presence of a methyl group at the 3-position (entries 6 and 5) suggesting that the inductive effect of the phenylsulfonyl group is dominant in stabilising the semiquinone. The effects of acetyl, benzoyl, pivaloyl and methoxycarbonyl substituents at the 3-position are similar, with increments due to the phenylsulfonyl group ranging from 228 to 322 mV (entries 8, 7; 10, 9; 12, 11; 14, 13 respectively).

The first half-wave reduction potential of 2,6-bisphenylsulfonyl-1,4-benzoquinone (entry 15) is 649 mV above that of 1,4-benzoquinone (entry 1), and 288 mV above that of phenylsulfonyl-1,4-benzoquinone (entry 2), effects which in each case are *ca.* 70 mV less than additive. The presence of methyl groups at both the 3- and 5-positions (entry 19) of the bisphenylsulfonylquinone reduces the increment over the parent (entry 18) to 564 mV, in line with the effect of an adjacent methyl group in the monophenylsulfonyl series (entries 6, 5 *vs.* 2, 1); the situation with 3,6-dimethyl-2,5-bisphenylsulfonyl-1,4-benzoquinone (entries 17, 16) is similar. 2,3-Bisphenylsulfonyl-1,4-benzoquinone did not give a satisfactory voltammagram.

The second half-wave reduction potential follows a similar pattern, although some of the quinones (entries 2,7,15,17) failed to give meaningful waves.

The phenylsulfonyl group thus stabilises the semiquinone ($Q^{\bullet -}$) to an extent which is only slightly less than that of a cyano group (cyano-1,4-benzoquinone has $E_{\frac{1}{2}}^1$ + 10 mV in dimethylformamide[22]), and the first half-wave reduction potential of phenylsulfonyl-1,4-benzoquinone (−40 mV) is very similar to that of 2,5-bismethoxycarbonyl-1,4-benzoquinone (−32 mV in dimethylformamide[22]). The phenylsulfonylquinones therefore complement the already extensive range of quinones having potentially useful redox properties.

* The products were racemic; only one enantiomer is shown.

Experimental

Organic solutions were dried over sodium sulfate. Reactions involving quinones were carried out with the exclusion of light from the reaction vessel. Products were crystallized from toluene unless otherwise stated. *J* values are given in Hz.

General Procedure for the Preparation of Phenylsulfonylhydroquinones.—Phenylsulfonylhydroquinone. A solution of 1,4-benzoquinone (5.02 g, 46.48 mmol) and trifluoroacetic acid (3.5 cm^3, 47.13 mmol) in dichloromethane (65 cm^3) was shaken at room temperature with a solution of sodium benzenesulfinate (7.94 g, 48.41 mmol) in water (45 cm^3) for 4 h: the quinone solution was decolourised. The precipitate was collected by filtration, washed with water and dried under reduced pressure. The layers of the two-phase filtrate were separated and the organic layer was dried. Solvent removal gave a creamy-white solid. Recrystallisation from toluene gave the hydroquinone as white needles (11.05 g, 95%), m.p. 199–200 °C (lit.,[2] 196 °C); ν_{max}(Nujol)/cm^{-1} 3255br, 1505m, 1370s, 1295s, 1225m, 1145s and 1090m; δ_H[60 MHz; $(CD_3)_2CO$] 8.52 (br s, removed by D_2O, 1- and 4-OH), 8.04 (m, 2′-H and 6′-H), 7.65 (m, 3′-H, 4′-H and 5′-H), 7.37 (d, *J* 2.5, 3-H), 7.09 (dd, J_1 9, J_2 2.5, 5-H) and 6.85 (d, *J* 9, 6-H); *m/z* 250 (M^+, 100%).

2,3-*Dimethyl-5-phenylsulfonylhydroquinone.* Needles (78%), m.p. 197–198 °C (lit.,[19] 196–198 °C); ν_{max}(Nujol)/cm^{-1} 1680w, 1310m, 1295m and 1270s; δ_H[60 MHz; $(CD_3)_2CO$] 8.77 (s, removed by D_2O, 1-OH), 8.20 (br s, removed by D_2O, 4-OH), 7.96 (m, 2′-H and 6′-H), 7.65 (m, 3′-H, 4′-H and 5′-H), 7.09 (s, 6-H) and 2.14 (s, 2-Me and 3-Me); *m/z* 278 (M^+, 27%), 77 (96) and 51 (100).

2,5-*Dimethyl-3-phenylsulfonylhydroquinone.* Needles (79%), m.p. 154–154.5 °C (lit.,[19] 160–160.5 °C); ν_{max}(Nujol)/cm^{-1} 1710w, 1600w, 1570s and 1370m; δ_H[60 MHz; $(CD_3)_2CO$] 10.26 (br s, removed by D_2O, 4-OH), 8.15–7.33 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H and 1-OH), 7.03 (s, 6-H) and 2.17 (s, 2-Me and 5-Me); *m/z* 278 (M^+, 93%) and 77 (100).

2,6-*Dimethyl-3-phenylsulfonylhydroquinone.* Needles (84%), m.p. 147–148.5 °C (lit.,[19] 147.5–149 °C); ν_{max}(Nujol)/cm^{-1} 3580sh, 1470s, 1365m, 1365m, 1235s and 1205s; δ_H[60 MHz; $(CD_3)_2CO$] 9.92 (br s, removed by D_2O, 4-OH), 8.12–7.43 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H and 1-OH), 6.74 (s, 5-H) and 2.23 (s, 2-Me and 6-Me); *m/z* 278 (M^+, 70%) and 77 (100).

2,3,5-*Trimethyl-6-phenylsulfonylhydroquinone.* Needles, (82%), m.p. 148–149 °C (lit.,[19] 148–149 °C); ν_{max}(Nujol)/cm^{-1} 3260br, 1445m, 1410m and 1200s; δ_H[60 MHz; $(CD_3)_2CO$] 8.17–7.76 (m, 2′-H, 6′-H and 1-OH), 7.76–7.29 (3′-H, 4′-H, 5′-H and 4-OH), 2.25 (s, 5-Me) and 2.19 (s, 2-Me and 3-Me); *m/z* 292 (M^+, 52%) and 40 (100).

2-*Phenylsulfonylnaphthalene*-1,4-*diol.* Needles (68%), m.p. 178–179.5 °C (lit.,[15] 178 °C); ν_{max}(Nujol)/cm^{-1} 3415sh, 1450s, 1310m and 1270s; δ_H[300 MHz; $(CD_3)_2CO$] 9.92 (br s, removed by D_2O, 4-H), 8.47 (d, *J* 7.5, 8-H), 8.33 (d, *J* 7.5, 5-H), 8.16 (m, 2′-H and 6′-H), 7.92–7.70 (m, 3′-H, 4′-H, 5′-H, 6′-H and 7-H) and 7.09 (s, 3-H); *m/z* 300 (M^+, 100%).

2-*Phenylsulfonylanthracene*-1,4-*diol.* From 1,4-anthraquinone (0.81 g, 3.87 mmol), trifluoroacetic acid (1 cm^3, 13.46 mmol) in dichloromethane (30 cm^3) and sodium benzenesulfinate (1.99 g, 12.18 mmol) in water (40 cm^3). The *title compound* formed pale-yellow needles (0.77 g, 57%), m.p. 203–204 °C (Found: C, 68.6; H, 4.1; S, 9.0. $C_{20}H_{14}O_4S$ requires: C, 68.6; H, 4.0; S, 9.1%); ν_{max}(Nujol)/cm^{-1} 3670sh, 1690m, 1525m, and 1200s; δ_H[90 MHz; $(CD_3)_2CO$] 10.33 (br s, removed by D_2O, 1- and 4-OH), 8.95 (s, 9-H), 8.81 (s, 10-H), 8.40–7.95 (m, 5-H, 8-H, 2′-H and 6′-H), 7.85–7.45 (m, 7-H, 6-H, 3′-H, 4′-H and 5′-H) and 7.13 (s, 3-H); *m/z* 350 (M^+, 15%) and 208 [$(M - HSO_2Ph)^+$, 100].

Reaction Between Benzenesulfinic Acid and Methyl-1,4-*benzoquinone.*—Methyl-1,4-benzoquinone (0.56 g, 4.61 mmol), trifluoroacetic acid (0.39 cm^3, 5.16 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.85 g, 5.16 mmol) in water (10 cm^3) afforded a white solid (1.15 g). PLC (4:1, PhMe–MeOH; silica) of this solid (11 mg) gave (a) 2-methyl-6-phenylsulfonylhydroquinone (5 mg) R_f 0.54), m.p. 183–186 °C (lit.,[19] 189–191 °C); ν_{max}(CH_2Cl_2)/cm^{-1} 3580b, 3050w, 1275m, 1255s and 1200s; δ_H[300 MHz; $(CD_3)_2CO$] 8.88 (s, removed by D_2O, 1-OH), 8.48 (s, removed by D_2O, 4-OH), 8.16 (m, 2′-H and 6′-H), 7.14 (m, 3′-H, 4′-H and 5′-H), 7.20 (d, *J* 3, 5-H), 7.10 (d, *J* 3, 3-H) and 2.27 (s, Me); *m/z* 264 (M^+, 100%); and (b) 2-methyl-5-phenylsulfonylhydroquinone (contaminated with a small amount of 2-methyl-6-phenylsulfonylhydroquinone) (4.2 mg) (R_f 0.38), m.p. 158–164 °C; ν_{max}(CH_2Cl_2)/cm^{-1} 3580br, 3050m and 1275m; δ_H[300 MHz; $(CD_3)_2CO$] 8.85 (s, removed by D_2O, 1-OH), 8.44 (s, removed by D_2O, 4-OH), 8.14 (m, 2′-H and 6′-H), 7.79 (m, 3′-H, 4′-H and 5′-H), 7.41 (s, 6-H), 6.89 (s, 3-H) and 2.27 (s, Me) (together with lines due to the 5-phenylsulfonyl isomer); *m/z* 264 (M^+, 100%).

Reaction Between Benzenesulfinic Acid and tert-*Butyl*-1,4-*benzoquinone.*—*tert*-Butyl-1,4-benzoquinone (0.12 g, 0.72 mmol), trifluoroacetic acid (0.067 cm^3, 0.90 mmol) in dichloromethane (5 cm^3) and sodium benzenesulfinate (0.15 g, 0.90 mmol) in water (5 cm^3) gave 2-tert-*butyl*-6-*phenylsulfonylhydroquinone* (0.15 g, 76%) as white plates m.p. 147.5–149 °C (Found: C, 62.25; H, 5.9; S, 10.4. $C_{16}H_{18}O_4S$ requires: C, 62.75; H, 5.9; S, 10.5%); ν_{max}(CH_2Cl_2)/cm^{-1} 3320br, 1445m, 1430m, 1295m and 1250m; δ_H[60 MHz; $(CD_3)_2CO$] 9.26 (br s, removed by D_2O, 1-OH), 7.96 (m, 2′-H, 6′-H and 4-OH), 7.60 (m, 3′-H, 4′-H and 5′-H), 7.17 (d, *J* 3, 5-H), 7.07 (d, *J* 3, 3-H) and 1.34 (s, Bu^t); *m/z* (M^+, 67%) and 291 [$(M - Me)^+$, 100%]. The material recovered by removal of the solvent from the mother liquor had spectroscopic data consistent with it being a mixture of 2-*tert*-butyl-6-phenylsulfonylhydroquinone and 2-*tert*-butyl-5-phenylsulfonylhydroquinone; the latter was not isolated.

Reaction Between Benzenesulfinic Acid and Trifluoromethyl-1,4-*benzoquinone.*—Trifluoromethyl-1,4-benzoquinone (0.20 g, 1.16 mmol), trifluoroacetic acid (0.09 cm^3, 1.34 mmol) in dichloromethane (5 cm^3) and sodium benzenesulfinate (0.21 g, 1.26 mmol) in water (5 cm^3) afforded a white solid (0.31 g). PLC (4:1, PhMe–MeOH; silica) of this (10 mg) gave (a) 6-*phenylsulfonyl*-2-*trifluoromethylhydroquinone* (3.8 mg) (R_f 0.58), m.p. 138–139.5 °C (Found: M^+, 318.0180. $C_{13}H_9F_3O_4S$ requires *M*, 318.0174); ν_{max}(CH_2Cl_2)/cm^{-1} 3540br, 1470m and 1325m; δ_H[300 MHz; $(CD_3)_2CO$] 9.34–9.00 (br s, removed by D_2O, 1-OH), 8.23 (m, 2′-H and 6′-H), 7.87 (m, 3′-H, 4′-H and 5′-H and 1-OH), 7.64 (d, *J* 3, 5-H) and 7.49 (d, *J* 3, 3-H); *m/z* 318 (M^+, 100%); (b) 5-*phenylsulfonyl*-2-*trifluoromethylhydroquinone* (1.7 mg) (R_f 0.32), m.p. 164–166 °C (Found: M^+, 318.0180. $C_{13}H_9F_3O_4S$ requires *M*, 318.0174); ν_{max}(CH_2Cl_2)/cm^{-1} 3300br, 1450m and 1310m; δ_H[300 MHz; $(CD_3)_2CO$] 9.45 (br s, removed by D_2O, 4-OH), 8.20 (m, 2′-H and 6′-H), 7.82 (m, 3′-H, 4′-H, 5′-H and 1-OH), 7.84 (s, 6-H) and 7.32 (s, 3-H); *m/z* 318 (M^+, 100%).

Reaction Between Benzenesulfinic Acid and Methoxy-1,4-*benzoquinone.*—Methoxy-1,4-benzoquinone (0.21 g, 1.49 mmol), trifluoroacetic acid (0.137 cm^3, 1.84 mmol) in dichloromethane (5 cm^3) and sodium benzenesulfinate (0.29 g, 1.77 mmol) in water (5 cm^3) afforded a white solid (0.38 g). PLC (4:1, PhMe–MeOH; silica) of this (11 mg) gave (a) 2-*methoxy*-5-*phenylsulfonylhydroquinone* (9 mg) (R_f 0.55) m.p. 160–161.5 °C (Found: M^+, 280.0411. $C_{13}H_{12}O_5S$ requires *M*, 280.0405); ν_{max}-(CH_2Cl_2)/cm^{-1} 3340br, 1630m, 1495s, 1440m, 1380m and 1235m; δ_H[60 MHz; $(CD_3)_2CO$] 9.11 (br s, removed by D_2O, 4-OH), 8.82 (m, 2′-H and 6′-H), 8.18 (m, 3′-H, 4′-H, 5′-H and 1-OH), 7.35 (s, 6-H), 6.70 (s, 3-H) and 3.99 (s, Me); *m/z* 280 (M^+,

100%); (b) 2-*methoxy*-6-*phenylsulfonylhydroquinone* contaminated with a small amount of 2-methoxy-5-phenylsulfonylhydroquinone (1 mg) (R_f 0.16), m.p. 211–214 °C (Found: M^+, 280.0403. $C_{13}H_{12}O_5S$ requires M, 280.0405); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3400br, 1600m and 1200s; δ_H[300 MHz; $(CD_3)_2CO$] 8.61 (br s, removed by D_2O, 1-OH), 8.28 (br s, removed by D_2O, 4-OH), 8.23 (m, 2′-H and 6′-H), 7.84 (m, 3′-H, 4′-H and 5′-H), 7.23 (d, *J* 3, 5-H), 6.96 (d, *J* 3, 3-H) and 4.00 (s, Me) together with lines due to the other isomer; *m*/*z* 280 (M^+, 51%) and 83 (100).

2-*Acetyl*-3-*phenylsulfonylhydroquinone*.—Acetyl-1,4-benzoquinone (0.61 g, 4.10 mmol), trifluoroacetic acid (0.383 cm^3, 5.16 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.85 g, 5.15 mmol) in water (10 cm^3) gave 2-*acetyl*-3-*phenylsulfonylhydroquinone* (1.22 g, 68%) as white prisms, m.p. 182–183 °C (Found: C, 57.3; H, 4.2; S, 10.9. $C_{14}H_{12}O_5S$ requires: C, 57.5; H, 4.1 S, 11.0%); ν_{max}(Nujol)/cm^{-1} 3370br, 1680s, 1445s, 1375m and 1300m; δ_H[60 MHz; $(CD_3)_2CO$] 8.13–7.81 (m, 2′-H and 6′-H), 7.70–7.31 (m, 3′-H, 4′-H, 5′-H, 1-OH and 4-OH), 6.96 (d, *J* 9.3, 6-H or 5-H), 6.76 (d, *J* 9.3, 5-H or 6-H) and 2.52 (s, Me); *m*/*z* 292 (M^+, 41%) and 43 (100).

2-*Benzoyl*-3-*phenylsulfonylhydroquinone*.—Benzoyl-1,4-benzoquinone (0.57 g, 2.70 mmol), trifluoroacetic acid (0.245 cm^3, 3.30 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.54 g, 3.31 mmol) in water (10 cm^3) gave the *hydroquinone* as white prisms (0.82 g, 85%), m.p. 207–210 °C (Found: C, 65.7; H, 3.9; S, 8.8. $C_{19}H_{14}O_5S$ requires: C, 64.4; H, 3.95; S, 9.0%); ν_{max}(Nujol)/cm^{-1} 3140br, 1660s, 1600m, 1375m, 1585m, 1450m, 1320s and 1300s; δ_H[60 MHz; $(CD_3)_2CO$] 8.73–7.33 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 2″-H, 3″-H, 4″-H, 5″-H, 6″-H, 1-OH and 4-OH), 7.20 (d, *J* 9.3, 6-H or 5-H) and 6.96 (d, *J* 9.3, 5-H or 6-H); *m*/*z* 354 (M^+, 56%) and 77 (100).

Pivaloyl-1,4-*benzoquinone*.—Ammonium cerium(IV) nitrate (5.60 g, 10.22 mmol) in water (60 cm^3) was added over 20 min to a stirred solution of pivaloylhydroquinone dimethyl ether (0.63 g, 2.84 mmol) in acetonitrile (10 cm^3). This solution was stirred for 12 h at room temperature. After extraction with dichloromethane (3 × 25 cm^3), washing of the combined extracts with water (3 × 50 cm^3), drying and solvent removal, crystallisation from light petroleum (b.p. 60–80 °C) gave pivaloyl-1,4-benzoquinone (0.32 g, 57%), as orange–yellow needles, m.p. 74–75 °C (lit.,[20] 75–75.5 °C).

3-*Phenylsulfonyl*-2-*pivaloylhydroquinone*.—From pivaloyl-1,4-benzoquinone (0.29 g, 1.53 mmol), trifluoroacetic acid (0.133 cm^3, 1.78 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.29 g, 1.78 mmol) in water (10 cm^3). Recrystallisation from cyclohexane gave the *hydroquinone* as white needles (0.34 g, 66%), m.p. 101.5–104 °C (Found: C, 61.2; H, 5.5; S, 9.3. $C_{17}H_{18}O_5S$ requires: C, 61.1; H, 5.4, S, 9.6%); ν_{max}(Nujol)/cm^{-1} 3320br, 1680m, 1470m, 1435s, 1325m and 1225m; δ_H[60 MHz; $(CD_3)_2CO$] 8.16–7.90 (m, 2′-H and 6′-H), 7.74–7.38 (m, 3′-H, 4′-H, 5′-H and 1-OH), 7.17 (d, *J* 8.7, 6-H or 5-H), 6.85 (d, *J* 8.7, 5-H or 6-H), 1.36 (s, Bu^{t}Me) and 1.25 (s, Bu^{t}Me); *m*/*z* 334 (M^+, 4%) and 277 (100).

2-*Methoxycarbonyl*-3-*phenylsulfonylhydroquinone*.—Methoxycarbonyl-1,4-benzoquinone (0.26 g, 1.56 mmol), trifluoroacetic acid (0.137 cm^3, 1.84 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.30 g, 1.83 mmol) in water (10 cm^3) gave the *hydroquinone* as white prisms (0.40 g, 84%), m.p. 158.5–160 °C (Found: C, 54.9; H, 3.95; S, 10.35. $C_{14}H_{12}O_6S$ requires: C, 54.5; H, 3.9; S, 10.39%); ν_{max}(Nujol)/cm^{-1} 3690br, 3300br, 1700s, 1460m and 1345m; δ_H[60 MHz; $(CD_3)_2CO$] 8.81 (br s, removed by D_2O, 4-OH), 8.05 (m, 2′-H and 6′-H), 7.63 (m, 3′-H, 4′-H, 5′-H and 1-OH), 7.18 (d, *J* 10.5, 6-H or 5-H), 6.91 (d, *J* 10.5, 5-H or 6-H) and 3.88 (s, Me); *m*/*z* 292 (M^+, 10%) and 276 [(M − MeOH)$^+$, 100].

2,6-*Bisphenylsulfonylhydroquinone*.—Phenylsulfonyl-1,4-benzoquinone (0.41 g, 1.66 mmol), trifluoroacetic acid (0.154 cm^3, 2.09 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.34 g, 2.08 mmol) in water (10 cm^3) afforded the *hydroquinone* as white prisms (0.30 g, 46%) m.p. 179–180 °C (Found: C, 55.2; H, 3.5; S, 16.4. $C_{18}H_{14}O_6S_2$ requires: C, 55.4; H, 3.6; S, 16.4%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3220br, 3070m, 1450m and 1200s; δ_H[60 MHz; $(CD_3)_2CO$] 10.52 (s, removed by D_2O, 1-OH), 8.14–7.75 (m, 2′-H, 6′-H, 2″-H and 6″-H), 7.75–7.47 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H, 5″-H and 4-OH) and 7.38 (m, 3-H and 5-H); *m*/*z* 390 (M^+, 100%). The layers of the two-phase filtrate were separated and the organic layer was washed with water, dried and the solvent removed. Recrystallisation gave 2,3-bisphenylsulfonylhydroquinone as white prisms (0.31 g, 48%), m.p. 174–175 °C.

2,3-*Bisphenylsulfonylhydroquinone*.—Phenylsulfonyl-1,4-benzoquinone (0.40 g, 1.60 mmol), trifluoroacetic acid (0.48 cm^3, 6.47 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.28 g, 1.70 mmol) in water (10 cm^3) gave the *hydroquinone* as white prisms (0.48 g, 67%); m.p. 174–175.5 °C (Found: C, 55.4; H, 3.6; S, 16.4. $C_{18}H_{14}O_6S_2$ requires: C, 55.4; H, 3.6; S, 16.4%); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3220br, 1450s, 1315m and 1250m; δ_H[60 MHz; $(CD_3)_2CO$] 10.59 (s, removed by D_2O, 1-OH and 4-OH), 8.11–7.46 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 2″-H, 3″-H, 4″-H, 5″-H and 6″-H) and 7.37 (s, 5-H and 6-H); *m*/*z* 390 (M^+, 20%) and 77 (100).

2,5-*Dimethyl*-3,6-*bisphenylsulfonylhydroquinone*.—2,5-Dimethyl-3-phenylsulfonyl-1,4-benzoquinone (0.82 g, 0.66 mmol), trifluoroacetic acid (0.06 cm^3, 0.80 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.13 g, 0.78 mmol) in water (10 cm^3) gave the *hydroquinone* as white prisms (0.24 g, 93%), m.p. 246.5–247.5 °C (Found: C, 57.55; H, 4.4; S, 15.0. $C_{20}H_{18}O_6S_2$ requires: C, 57.4; H, 4.3; S, 15.3%); ν_{max}(Nujol)/cm^{-1} 3260sh, 3200sh, 1390m, 1370m and 1160s; δ_H[300 MHz; $(CD_3)_2CO$] 8.15 (m, 2′-H, 6′-H, 2″-H, 6″-H, 1-OH and 4-OH), 8.00–7.80 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H and 5″-H) and 2.38 (s, 2-Me and 5-Me); *m*/*z* 418 (M^+, 100%).

2,6-*Dimethyl*-3,5-*bisphenylsulfonylhydroquinone*.—2,6-Dimethyl-3-phenylsulfonyl-1,4-benzoquinone (0.27 g, 1.32 mmol), trifluoroacetic acid (0.121 cm^3, 1.63 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.27 g, 1.63 mmol) in water (10 cm^3) gave the *hydroquinone* as white needles (0.47 g, 85%), m.p. 177–178 °C (Found: C, 57.3; H, 4.3; S, 15.2. $C_{20}H_{18}O_6S_2$ requires: C, 57.4; H, 4.3; S, 15.3%); ν_{max}(Nujol)/cm^{-1} 3450sh, 3150sh, 1565m, 1370m and 1310m; δ_H[300 MHz; $(CD_3)_2CO$] 8.06 (m, 2′-H, 6′-H, 2″-H, 6″-H), 7.82 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H and 5″-H, 1-OH and 4-OH) and 2.66 (s, 2-Me and 6-Me); *m*/*z* 418 (M^+, 47%) and 278 (100).

2,3-*Dimethyl*-5,6-*bisphenylsulfonylhydroquinone*.—2,3-Dimethyl-5-phenylsulfonyl-1,4-benzoquinone (0.34 g, 1.24 mmol), trifluoroacetic acid (0.184 cm^3, 2.49 mmol) in dichloromethane (10 cm^3) and sodium benzenesulfinate (0.41 g, 2.49 mmol) in water (10 cm^3) gave the *hydroquinone* as white needles (0.25 g, 67%), m.p. 160–161 °C (Found: C, 57.1; H, 4.2; S, 15.6. $C_{20}H_{18}O_6S_2$ requires: C, 57.4; H, 4.3; S, 15.3%); ν_{max}(Nujol)/cm^{-1} 3010sh, 1675s and 1330s; δ_H[60 MHz; $(CD_3)_2CO$] 7.88–7.42 (m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H, 2″-H, 3″-H, 4″-H, 5″-H, 6″-H, 1- and 4-OH) and 1.94 (s, 2-Me and 3-Me); *m*/*z* 418 (M^+, 9%) and 77 (100).

General Procedure for the Preparation of Phenylsulfonylquinones using Silver(I) *Oxide*.—*Phenylsulfonyl*-1,4-*benzoquinone*.

Phenylsulfonylhydroquinone (10.24 g), benzene (150 cm^3), silver(I) oxide (29.23 g) and anhydrous sodium sulfate (27.5 g) were shaken together at room temperature for 12 h. The mixture was filtered through Celite, the solvent was removed and the residue was crystallised from cyclohexane affording phenylsulfonyl-1,4-benzoquinone as yellow needles (8.87 g, 87%), m.p. 139–140 °C (lit.,[18] 139 °C); ν_{max}(Nujol)/cm^{-1} 1665s, 1460m and 1380w; δ_H(60 MHz; $CDCl_3$) 8.05 (m, 2′-H and 6′-H), 7.58 (m, 3-H, 3′-H, 4′-H and 5′-H) and 6.74 (m, 5-H and 6-H); *m/z* 250 [(M + 2)$^+$, 8)], 248 (M^+, 5) and 77 (100).

2,5-*Dimethyl*-3-*phenylsulfonyl*-1,4-*benzoquinone*. 2,5-Dimethyl-3-phenylsulfonylhydroquinone (0.51 g) and silver(I) oxide (2.92 g) gave the *quinone* as yellow needles (0.34 g, 68%), m.p. 145.5–147 °C (Found: C, 60.6; H, 4.3; S, 11.4. $C_{14}H_{12}O_4S$ requires: C, 60.8; H, 4.3; S, 11.5%); ν_{max}(Nujol)/cm^{-1} 1670s, 1590w, 1330s, 1290m, 1180m and 1160s; δ_H(220 MHz; $CDCl_3$) 8.08 (m, 2′-H and 6′-H), 7.80–7.50 (m, 3′-H, 4′-H and 5′-H), 6.72 (s, with fine splitting, 6-H), 2.65 (s, 2-Me) and 1.95 (d, *J* 1.15, 5-Me); *m/z* 276 (M^+, 3%) and 67 ($C_4H_3O^+$, 100).

2,6-*Dimethyl*-3-*phenylsulfonyl*-1,4-*benzoquinone*. 2,6-Dimethyl-3-phenylsulfonylhydroquinone (0.89 g) and silver(I) oxide (2.84 g) afforded the *quinone* as yellow needles (0.76 g, 85%), m.p. 122–123.5 °C (Found: C, 60.7; H, 4.3; S, 11.95. $C_{14}H_{12}O_4S$ requires: C, 60.8; H, 4.3; S, 11.6%); ν_{max}(Nujol)/cm^{-1} 1695w, 1660s, 1520m and 1355m; δ_H(60 MHz; $CDCl_3$) 8.26–7.76 (m, 2′-H and 6′-H), 7.76–7.16 (m, 3′-H, 4′-H and 5′-H), 6.42 (s, with fine splitting, 5-H), 2.67 (d, *J* 1.5, 2-Me) and 2.02 (s, 6-Me); *m/z* 276 (M^+, 1%) and 67 ($C_4H_3O^+$, 100).

2,3-*Dimethyl*-5-*phenylsulfonyl*-1,4-*benzoquinone*. 2,3-Dimethyl-5-phenylsulfonylhydroquinone (0.57 g) and silver(I) oxide (1.68 g) gave the *quinone* as yellow needles (0.45 g, 80%), m.p. 152–154 °C (Found: C, 60.7; H, 4.4; S, 11.6. $C_{14}H_{12}O_4S$ requires: C, 60.8; H, 4.3; S, 11.6%); ν_{max}(Nujol)/cm^{-1} 1655s, 1165s and 1090m; δ_H(60 MHz; $CDCl_3$) 8.08 (m, 2′-H and 6′-H), 7.59 (m, 3′-H, 4′-H and 5′-H), 7.34 (s, 6-H) and 2.00 (s, 2-Me and 6-Me); *m/z* 276 (M^+, 1%) and 212 [(M − SO_2)$^+$, 100].

2,3,5-*Trimethyl*-6-*phenylsulfonyl*-1,4-*benzoquinone*. 2,3,5-Trimethyl-6-phenylsulfonylhydroquinone (0.41 g) and silver(I) oxide (1.76 g) gave the *quinone* as yellow plates (0.28 g, 70%), m.p. 133–134 °C (Found: C, 62.2; H, 4.9; S, 11.5. $C_{15}H_{14}O_4S$ requires: C, 62.1; H, 4.8; S, 11.0%); ν_{max}(Nujol)/cm^{-1} 1655s and 1320m; δ_H(60 MHz; $CDCl_3$) 8.16–7.81 (m, 2′-H and 6′-H), 7.71–7.22 (m, 3′-H, 4′-H and 5′-H), 2.65 (s, 5-Me) and 1.96 (m, 2-Me and 3-Me); *m/z* 292 [(M + 2)$^+$, 7%], 290 (M^+, 2) and 67 ($C_4H_3O^+$, 100).

2-*Phenylsulfonyl*-1,4-*naphthoquinone*. 2-Phenylsulfonyl-1,4-naphthohydroquinone (0.55 g) and silver(I) oxide (1.48 g) afforded the quinone as yellow–green needles (0.28 g, 55%), m.p. 190–191 °C (lit.,[20] 190 °C); ν_{max}(Nujol)/cm^{-1} 1670s, 1590m, 1330m and 1170s; δ_H(300 MHz; $CDCl_3$) 8.21 (d, *J* 7.2, 2′-H and 6′-H), 8.41 (dd, J_1 6, J_2 3, 5-H), 8.09 (dd, J_1 6, J_2 3, 8-H), 7.91 (s, 3-H), 7.85 (dd, J_1 6, J_2 3, 6-H and 7-H), 7.70 (t, *J* 7.2, 4′-H) and 7.64 (t, *J* 7.3, 3′-H and 5′-H); *m/z* 300 [(M + 2)$^+$, 22%] and 234 [(M − SO_2)$^+$, 100].

2-*Acetyl*-3-*phenylsulfonyl*-1,4-*benzoquinone*. 2-Acetyl-3-phenylsulfonylhydroquinone (0.79 g) and silver(I) oxide (2.26 g) afforded the *quinone* as an orange solid (0.40 g, 62%), m.p. 142–145 °C which could not be purified further; ν_{max}(CH_2Cl_2)/cm^{-1} 1710m, 1670s, 1330m and 1270m; δ_H(60 MHz; $CDCl_3$) 8.17–7.85 (m, 2′-H and 6′-H), 7.73–7.37 (m, 3′-H, 4′-H and 5′-H), 6.81 (d, *J* 10.7, 5-H or 6-H), 6.63 (d, *J* 10.7, 6-H or 5-H) and 2.60 (s, Me); *m/z* 290 (M^+, 26%) and 43 (100).

2-*Benzoyl*-3-*phenylsulfonyl*-1,4-*benzoquinone*. 2-Benzoyl-3-phenylsulfonylhydroquinone (0.67 g) and silver(I) oxide (2.26 g) afforded the quinone as an orange solid (0.51 g, 77%), m.p. 163.5–167 °C, which could not be purified further; ν_{max}(CH_2Cl_2)/cm^{-1} 1685m, 1670s, 1450m, 1335m and 1270m; δ_H[60 MHz; $(CD_3)_2CO$] 8.36–7.81 (m, 2′-H, 6′-H, 2″-H and 6″-H), 7.81–7.40 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H and 5″-H), 7.01 (d, *J* 9.3, 5-H or 6-H) and 6.63 (d, *J* 9.3, 6-H or 5-H); *m/z* 352 (M^+, 2%) and 105 (100).

3-*Phenylsulfonyl*-2-*pivaloyl*-1,4-*benzoquinone*. 3-Phenylsulfonyl-2-pivaloylhydroquinone (0.22 g) and silver(I) oxide (1.18 g) afforded the quinone as an orange solid (0.17 g, 77%), m.p. 47.5–59 °C, which could not be purified further; ν_{max}(CH_2Cl_2)/cm^{-1} 1700m, 1670s, 1330m and 1270m; δ_H(60 MHz; $CDCl_3$) 8.25–7.91 (m, 2′-H and 6′-H), 7.91–7.77 (m, 3′-H, 4′-H and 5′-H), 6.90 (d, *J* 10.7, 5-H or 6-H), 6.69 (d, *J* 10.7, 6-H or 5-H) and 1.37 (s, Bu^t, Me); *m/z* 332 (M^+, 26%) and 43 (100).

2-*Methoxycarbonyl*-3-*phenylsulfonyl*-1,4-*benzoquinone*. 2-Methoxycarbonyl-3-phenylsulfonylhydroquinone (0.23 g) and silver(I) oxide (2.65 g) afforded the *quinone* as yellow needles (0.15 g, 64%), m.p. 144.5–146 °C (Found: M^+, 306.0195. $C_{14}H_{10}O_6S$ requires *M*, 306.0198); ν_{max}(CH_2Cl_2)/cm^{-1} 1780s, 1670s, 1340m, 1305m and 1280m; δ_H(220 MHz; $CDCl_3$) 8.15 (m, 2′-H and 6′-H), 7.64 (m, 3′-H, 4′-H and 5″-H), 6.89 (d, *J* 10, 5-H or 6-H), 6.77 (d, *J* 10, 6-H or 5-H) and 4.07 (s, Me); *m/z* 306 (M^+, 28%) and 182 (100).

General Procedure for the Preparation of Phenylsulfonylbenzoquinones using Phenyliodine(III) *Bistrifluoroacetate*.—2,6-*Bisphenylsulfonyl*-1,4-*benzoquinone*. Phenyliodine(III) bistrifluoroacetate (0.14 g, 0.33 mmol) was added over 10 min to a solution of 2,6-bisphenylsulfonylhydroquinone (0.13 g, 0.32 mmol) in dichloromethane (30 cm^3) and the mixture was then stirred for 60 min. The solvent was removed and the solid was washed with light petroleum (b.p. 80–100 °C) and pumped at 0.05 mmHg until constant weight was obtained. Recrystallisation from benzene gave the *quinone* as orange prisms (0.10 g, 78%), m.p. 238–239 °C (Found: C, 55.8; H, 3.0; S, 16.6. $C_{18}H_{12}O_6S_2$ requires: C, 57.7; H, 3.1; S, 16.5%); $\nu_{max}CH_2Cl_2$)/cm^{-1} 1675m, 1665m, 1335m and 1275m; δ_H[300 MHz; $(CD_3)_2CO$] 8.17–7.85 (m, 2′-H, 6′-H, 2″-H and 6″-H) and 7.85–7.46 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H and 5″-H, 3-H and 5-H); δ_C(20.1 MHz; CD_2Cl_2 184.7 (C-1), 175.8 (C-4), 146.3 (C-2 and C-3), 137.9 (C-3, C-5, C-1′ and C-1″), 135.5 (C-4′ and C-4″) and 129.9 (C-2′, C-3′, C-5′, C-6′, C-2″, C-5″ and C-6″); *m/z* 388 (M^+, 2%) and 91 ($C_7H_7^+$, 100).

2,3-*Bisphenylsulfonyl*-1,4-*benzoquinone*. 2,3-Bisphenylsulfonylhydroquinone (0.16 g, 0.41 mmol) and phenyliodine(III) bistrifluoroacetate (0.18 g, 0.41 mmol) gave the *quinone* as orange prisms (0.13 g, 79%), m.p. 146–148 °C (Found: C, 55.4; H, 3.2; S, 16.6. $C_{18}H_{12}O_6S_2$ requires: C, 57.7; H, 3.1; S, 16.5%); ν_{max}-(CH_2Cl_2)/cm^{-1} 1670s, 1450m, 1335s and 1170s; δ_H[300 MHz; $(CD_3)_2CO$] 8.57–8.22 (m, 2′-H, 6′-H, 2″-H and 6″-H), 8.02 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H and 5″-H) and 6.94 (s, 5-H and 6-H); δ_C(20.1 MHz; CD_2Cl_2) 182.6 (C-1 and C-4), 149.4 (C-2 and C-3), 140.2 (C-1′ and C-1″), 136.7 (C-5 and C-6 or C-4′ and C-4″), 135.1 (C-4′ and C-4″ or C-5 and C-6), 130.5 (C-2′, C-6′, C-2″ and C-6″) and 129.3 (C-3′, C-5′, C-3″ and C-5″); *m/z* 388 (M^+, 10%) and 77 (100).

2,5-*Dimethyl*-3,6-*bisphenylsulfonyl*-1,4-*benzoquinone*. 2,5-Dimethyl-3,6-bisphenylsulfonylhydroquinone (0.19 g, 0.45 mmol) and phenyliodine(III) bistrifluoroacetate (0.20 g, 0.45 mmol) gave the *quinone* as yellow needles (0.17 g, 86%), m.p. 229–230 °C (Found: C, 57.85; H, 3.9; S, 15.1. $C_{20}H_{16}O_6S_2$ requires: C, 57.7; H, 3.8; S, 15.4%); ν_{max}(CH_2Cl_2)/cm^{-1} 1674s, 1600w, 1460s, 1325s and 1240m; δ_H(300 MHz; $CDCl_3$) 8.14 (m, 2′-H, 6′-H, 2″-H and 6″-H), 7.84–7.56 (m, 3′-H, 4′-H, 5′-H, 3″-H, 4″-H and 5″-H) and 2.64 (s, 2-Me and 5-Me); *m/z* 418 [(M + 2)$^+$, 95%], 416 (M^+, 2%) and 91 (C_7H_7, 100).

2,6-*Dimethyl*-3,5-*bisphenylsulfonyl*-1,4-*benzoquinone*. 2,6-Dimethyl-3,5-bisphenylsulfonylhydroquinone (0.25 g, 0.59 mmol) and phenyliodine(III) bistrifluoroacetate (0.28 g, 0.64 mmol) gave the *quinone* as yellow needles (0.20 g, 81%), m.p. 230–231 °C (Found: C, 57.7; H, 3.9; S, 15.6. $C_{20}H_{16}O_6S_2$ requires: C, 57.7; H,

3.8; S, 15.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1680w, 1655m, 1460s, 1375s and 1320s; δ_H(300 MHz; $CDCl_3$) 8.02 (m, 2'-H, 6'-H, 2''-H and 6''-H), 7.62 (m, 3'-H, 4'-H, 5'-H, 3''-H, 4''-H and 5''-H) and 2.68 (s, 2-Me and 6-Me); *m/z* 418 [$(M + 2)^+$, 58%], 416 (M^+, 1) and 77 (100).

2,3-*Dimethyl*-5,6-*bisphenylsulfonyl*-1,4-*benzoquinone*. 2,3-Dimethyl-5,6-bisphenylsulfonylhydroquinone (0.19 g, 0.45 mmol) and phenyliodine(III) bistrifluoroacetate (0.20 g, 0.45 mmol) gave the *quinone* as yellow needles (0.16 g, 84%), m.p. 249.5–251 °C (Found: C, 57.1; H, 4.4; S, 15.0.* $C_{20}H_{16}O_6S_2$ requires: C, 57.7; H, 3.8; S, 15.4%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3000w, 1675s, 1375s, 1330s and 1220s; δ_H(60 MHz; $CDCl_3$) 8.23–7.79 (m, 2'-H, 6'-H, 2''-H and 6''-H), 7.79–7.26 (m, 3'-H, 4'-H, 5'-H, 3''-H, 4''-H and 5''-H) and 1.99 (s, 2-Me and 3-Me); *m/z* 418 [$(M + 2)^+$, 1%] and 212 (100).

Diels–Alder Adducts

4a,5,8,8a-*Tetrahydro*-4a-*phenylsulfonyl*-5,8-*methano*-1,4-*naphthoquinone* **11** (R = H).—A solution of phenylsulfonyl-1,4-benzoquinone (0.59 g, 2.37 mmol) and cyclopentadiene (0.2 cm^3, 2.43 mmol) in dichloromethane (5 cm^3) was allowed to stand at room temperature for 2 h. Removal of the solvent followed by crystallisation from cyclohexane gave the *Diels–Alder adduct* as yellow needles (0.72 g, 97%), m.p. 114.5–116 °C (Found: C, 64.8; H, 4.5; S, 10.0. $C_{17}H_{14}O_4S$ requires: C, 65.0; H, 4.5; S, 10.2%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3060w, 1680s, 1310m, 1205m and 1150s; δ_H(60 MHz; $CDCl_3$) 7.67 (m, 2'-H, 3'-H, 4'-H, 5'-H and 6'-H), 6.50 (s, 2-H and 3-H), 6.18 (m, 6-H), 5.96 (m, 7-H), 4.11 (d, *J* 4, 8a-H), 3.66 (m, 8-H), 3.47 (m, 5-H), 2.39 (dm, *J* 9.3, 9-H *anti*) and 1.50 (dm, *J* 9.3, 9-H *syn*); *m/z* 314 (M^+, 2%) and 51 ($C_4H_3^+$, 100).

4a,5,8,8a-*Tetrahydro*-4a-*phenylsulfonyl*-1,4-*naphthoquinone* **12** (R = H).—Butadiene gas was bubbled into a solution of phenylsulfonyl-1,4-benzoquinone (0.30 g, 1.21 mmol) in dichloromethane (5 cm^3) at 0 °C for 3 min. The solution was warmed to room temperature and allowed to stand for 2 h. Removal of the solvent followed by crystallisation from cyclohexane gave the *Diels–Alder adduct* as yellow–green needles (0.29 g, 80%), m.p. 120–121.5 °C (Found: C, 63.5; H, 4.8; S, 10.65. $C_{16}H_{14}O_4S$ requires: C, 63.6; H, 4.6; S, 10.6%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3060w, 1685s, 1605m, 1450m, 1315s and 1200m; δ_H(60 MHz; $CDCl_3$) 7.73 (m, 2'-H, 3'-H, 4'-H, 5'-H and 6'-H), 6.79 (s, 2-H and 3-H), 5.71 (m, 6-H and 7-H), 3.57 (dd, J_1 10.5, J_2 8, 8a-H) and 3.15–1.94 (m, 5α-H, 5β-H, 8α-H and 8β-H); *m/z* 302 (M^+, 26%) and 77 (100).

4a,5,8,8a-*Tetrahydro*-5-*methyl*-4a-*phenylsulfonyl*-1,4-*naphthoquinone* **12** (R = Me).—A mixture of phenylsulfonyl-1,4-benzoquinone (0.62 g, 2.48 mmol) and (*E*)-penta-1,3-diene (0.25 cm^3, 2.51 mmol) in dichloromethane (5 cm^3) was allowed to stand at room temperature for 2 h. Removal of the solvent followed by crystallisation from cyclohexane gave the *Diels–Alder adduct* as yellow needles (0.75 g, 95%), m.p. 91–92 °C (Found: C, 64.5; H, 5.1; S, 10.2. $C_{17}H_{16}O_4S$ requires: C, 64.55; H, 5.1; S, 10.1%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3070w, 1705s, 1610m, 1450m and 1310s; δ_H(60 MHz; $CDCl_3$) 7.91 (m, 2'-H and 6'-H), 7.63 (m, 3'-H, 4'-H and 5'-H), 6.91 (d, *J* 10.5, 2-H or 3-H), 6.70 (d, *J* 10.5, 3-H or 2-H), 5.62 (m, 6-H and 7-H), 3.74 (dd, J_1 9.3, J_2 7, 8a-H), 2.71 (m, 5-H, 8α-H and 8β-H) and 0.99 (d, *J* 5, 5-Me); *m/z* 316 (M^+, 17%) and 77 (100).

4a,5,8,8a-*Tetrahydro*-2,3-*bisphenylsulfonyl*-5,8-*methano*-1,4-*naphthoquinone* **13**.—A mixture of 2,3-bisphenylsulfonyl-1,4-benzoquinone (0.16 g, 0.42 mmol) and cyclopentadiene (0.035 cm^3, 0.42 mmol) in dichloromethane (5 cm^3) was allowed to stand at room temperature for 1 h. Removal of the solvent followed by crystallisation from cyclohexane to give the *Diels–Alder adduct* as yellow needles (0.11 g, 60%), m.p. 155–159 °C (Found: C, 55.7; H, 4.0; S, 14.5.* $C_{23}H_{18}O_6S_2$ requires: C, 60.8; H, 4.0; S, 14.1%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1695m, 1665m, 1470s, 1440s, 1340m and 1305s; δ_H(60 MHz; $CDCl_3$) 8.30–7.98 (m, 2'-H, 6'-H, 2''-H and 6''-H), 7.76–7.36 (m, 3'-H, 4'-H, 5'-H, 3''-H, 4''-H and 5''-H), 6.07 (m, 6-H and 7-H), 3.40 (m, 4a-H, 8a-H, 5-H and 8-H) and 1.48 (m, 9-H *syn* and 9-H *anti*); *m/z* 454 (M^+, 1) and 51 ($C_4H_3^+$, 100%).

5,8-*Dihydro*-2-*phenylsulfonylnaphthalene*-1,4-*diol*.—A solution of 4a,5,8,8a-tetrahydro-4a-phenylsulfonyl-1,4-naphthoquinone (0.41 g, 1.34 mmol) in pyridine (10 cm^3) was allowed to stand at room temperature for 20 minutes. Removal of the solvent and crystallisation gave *the hydroquinone* as white prisms (0.37 g, 92%), m.p. 188.5–189.5 °C (Found: C, 63.8; H, 4.7; S, 11.0. $C_{16}H_{14}O_4S$ requires: C, 63.6; H, 4.6; S, 10.6%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3470sh, 3330sh, 1460s and 1380m; δ_H[60 MHz; $(CD_3)_2CO$] 7.99 (m, 2'-H and 6'-H), 7.63 (m, 3'-H, 4'-H and 5'-H, 1-OH and 4-OH), 7.08 (s, 3-H), 5.83 (6-H and 7-H) and 3.24 (s, 5α-H, 5β-H, 8α-H and 8β-H); *m/z* 302 (M^+, 94%) and 161 [$(M - SO_2Ph)^+$, 100].

Cyclic Voltammetry.—Measurements were made at ambient temperature over the range +1 V to −2 V using a Princeton Applied Research model 173 potentiostat for solutions of the quinones in dimethylformamide (Baker Chemical Co., analytical grade dried over 4 Å molecular sieves) containing tetrabutylammonium tetrafluoroborate (50 mmol dm^{-3}, Aldrich Chemical Co., crystallised from 4:1 water–methanol and dried over P_2O_5) as the supporting electrolyte, using a 28 mm^2 area glassy carbon electrode with platinum counter electrode and a saturated calomel reference electrode. Reproducibility was ±20 mV for $Q/Q^{\cdot-}$ and ± 40 mV for $Q^{\cdot-}/Q^{2-}$. Under these conditions ferrocene had a first half-wave reduction potential of +524 mV.

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