Reactions of *N*-sulfinylarylamines with 1,4-benzoquinone and 1,4-naphthoquinone: synthesis of *N*-aryl sulfinamoyl quinones and their hydrolysis to hydroxyquinones

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N-Sulfinylarylamines react with 1,4-naphthoquinone to give 2-(*N*-arylsulfinamoyl)-1,4-naphthoquinones. The reaction is believed to occur *via* an initial 2 + 2 cycloaddition of the N=S bond of the *N*-sulfinylamine with 1,4-naphthoquinone, followed by fragmentation of the 1,2-thiazetidine 1-oxide intermediate with a 1,3-H shift. *N*-Sulfinylarylamines add regiospecifically to 5-hydroxy-1,4-naphthoquinone to give 3-(*N*-arylsulfinamoyl)-5-hydroxy-1,4-naphthoquinones. 1,4-Benzoquinone reacts with three molecules of *N*-sulfinylarylamine to give adducts. Two molecules of *N*-sulfinylarylamine react with 1,4-benzoquinone as in the case of 1,4-naphthoquinone and the third molecule reacts at one of the C=O groups of the benzoquinone with the elimination of a molecule of SO_2. Hydrolysis of 2-(*N*-arylsulfinamoyl)-1,4-naphthoquinones with aqueous HCl gives 2-hydroxy-1,4-naphthoquinone.

Introduction

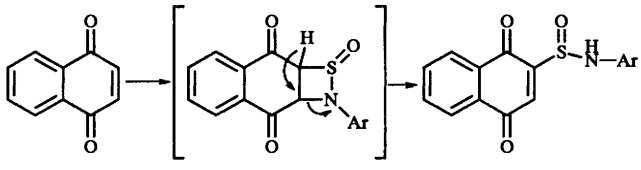
The cycloadditions of *N*-sulfinylamines such as PhN=S=O to 1,3-dienes yielding 1,2-thiazine *S*-oxides were discovered more than 40 years ago.[1] This 4 + 2 cycloaddition is the only widely studied reaction of *N*-sulfinylamines. Ring-opening reactions of 1,2-thiazine *S*-oxide products are also known and this has been used in the synthesis of the hydroxyamine units of *threo*- and *erythro*-sphingosine.[2] Apart from this 4 + 2 cycloaddition, a number of other reactions are also known for this versatile heterocumulene. *N*-Sulfinylarylamines react with a limited number of strained alkenes such as bicyclic nonenes in another 4 + 2 cycloaddition. In these reactions the N=S bond acts as a part of the diene. This second type of reaction is known only for a limited number of alkenes.[3-5]

Several groups have attempted to extend this reaction to a wider range of alkenes without success.[3,6,7] A third type of 4 + 2 cycloaddition is known with aromatic Schiff bases. In these reactions the N=S bond of the sulfinylamine also acts as the dienophile. The C=N bond of the Schiff base and the aromatic ring participate as the diene.[8] The product obtained is a thiazine oxide. *N*-Alkyl Schiff bases react by a completely different route in these reactions and this reaction has been explained as an initial 2 + 2 cycloaddition of the C=N of the Schiff base and the N=S of the sulfinylamine, followed by a ring opening of the intermediate.[8] Aromatic and aliphatic *N*-sulfinylamines are known to add smoothly to diphenyl and biphenylene ketene.[9] The products formed are stable and have been identified as substituted 1,2-thiazetidinone oxides. Stable 2 + 2 adducts are also formed in the reaction between highly reactive sulfonyl sulfinylamines and enol ethers.[10] The products formed in these reactions are 3-alkoxy-1,2-thiazetidine 1-oxides. *ortho*-Substituted *N*-sulfinylarylamines and *N*-sulfinyl-*tert*-butylamines are known to undergo 2 + 2 cycloaddition with aluminium halide σ-complexes of cyclobutadienes. The cycloadduct was not isolated in the reaction and the elimination of SO_2 gave a pyrrole as the product.[11]

Results and discussion

(a) (i) Reactions of *N*-sulfinylarylamines with 1,4-naphthoquinone

In our studies on *N*-sulfinylamines we have found that *N*-sulfinylarylamines react with 1,4-naphthoquinone when an equimolar mixture of *N*-sulfinylaniline and 1,4-naphthoquinone in benzene is kept in the dark for 2–3 days.[12] The solution turned deep red and the product was isolated by preparative plate chromatography. The product formed in the reaction between *N*-sulfinylaniline and 1,4-naphthoquinone was identified as the 2-(*N*-phenylsulfinamoyl)-1,4-naphthoquinone **2a**. The ^{1}H NMR spectrum of this product showed a singlet peak at δ 6.43 for 3-H and the corresponding C-3 carbon was found at δ 103.35 in the ^{13}C spectrum. The carbon proton connectivities of the structure were established by a selective proton decoupled ^{13}C NMR experiment. The IR spectrum showed absorptions at 1675, 1614, 1124 and 3360 cm^{-1} corresponding to the two C=O groups, S=O and NH groups. Seven other *N*-sulfinylarylamines (**1b–h**) also gave the corresponding 2-(*N*-arylsulfinamoyl)-1,4-naphthoquinones **2b–h**. Formation of these sulfinamoyl quinone adducts can be explained by an initial 2 + 2 cycloaddition of the N=S bond of the sulfinylamine and the quinone to give a thiazetidinone intermediate and, fragmentation of this intermediate with 1,3-H shift (Scheme 1).



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Ar—N=S=O

2a–h

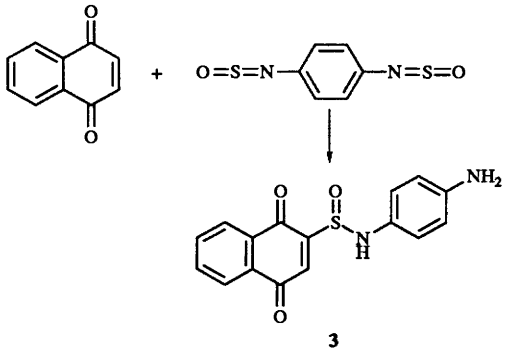
Ar	
1a Ph	**1e** *m*-Cl-C_6H_4
1b *o*-Me-C_6H_4	**1f** *p*-Cl-C_6H_4
1c *m*-Me-C_6H_4	**1g** *m*-NO_2-C_6H_4
1d *p*-Me-C_6H_4	**1h** 2-naphthyl

Scheme 1

This reaction was also attempted with 2 equivalents of *N*-sulfinylarylamine and the only product isolated was 2-(*N*-arylsulfinamoyl)-1,4-naphthoquinone. No product from the addition of two sulfinylamines was detected.

(ii) Reaction of 1,4-bis(*N*-sulfinylamino)benzene with 1,4-naphthoquinone. 1,4-Bis(*N*-sulfinylamino)benzene was allowed to react with 2 equivalents of 1,4-naphthoquinone in an

attempt to synthesise bis-naphthoquinone compounds. However, the reaction occurred only at one *N*-sulfinylamine group and the product isolated (**3**) results from the solvolysis of the other –N=S=O group during work-up and chromatography (Scheme 2). Similar behaviour has been observed by Hanson



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Scheme 2

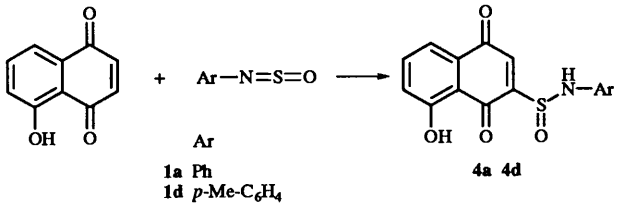
and Stone[5] 1,4-bis(*N*-sulfinylamino)benzene when treated with 1,4-epoxy-1,4-dihydronaphthalene.

(b) NMR study

In an attempt to identify the intermediate thiazetidinone, the reaction between 1,4-naphthoquinone and 4-methyl-*N*-sulfinylaniline **1d** was studied in an NMR tube in $CDCl_3$. Slow disappearance of the signals corresponding to the starting materials and appearance of the product signals were found during the course of the study of 2 weeks, and no other intermediate product peaks were seen. Therefore, we conclude that the first step of the reaction is the rate-determining step and that the fragmentation of the postulated thiazetidinone intermediate is a fast step.

(c) Regioselectivity in the addition of *N*-sulfinylarylamines to 5-hydroxy-1,4-naphthoquinone (juglone)

Reactions of two of the *N*-sulfinylarylamines (**1a** and **1d**) with 5-hydroxy-1,4-naphthoquinone were studied in order to determine the regiochemistry of the addition to an unsymmetrical 1,4-naphthoquinone (Scheme 3). The NMR



Ar

1a Ph

1d *p*-Me-C_6H_4

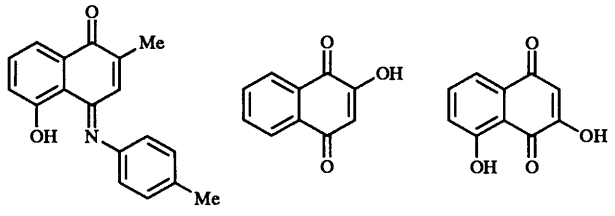
4a 4d

Scheme 3

spectra of the crude product from these reactions showed the formation of only one regioisomer. Regiochemical control in the Diels–Alder reactions of 5-hydroxy-1,4-naphthoquinone with unsymmetrical dienes is well documented[13,14] and explained in terms of the activation of the C-4 carbonyl by hydrogen bonding with the OH group.[15] Similar regioselectivity has been observed in the hetero Diels–Alder reaction with acrylaldehyde *N*,*N*-dimethylhydrazone as well.[16] Upon further studies on a wide range of dienes in the Diels–Alder reaction with juglone and related systems, Boeckman[17] has rationalised that good regioselectivity arises only with highly polarised dienes. Therefore, one could expect excellent regioselectivities in the 2 + 2 cycloaddition of the highly polarised N=S bond with alkenes. Polarization arguments predict that the product formed is the 3-(*N*-arylsulfinamoyl) isomer of 5-hydroxy-1,4-naphthoquinone. This was further confirmed by hydrolysing the product to give 2,8-dihydroxy-1,4-naphthoquinone. As far as we are aware this is the first example of regiospecific 2 + 2 cycloaddition to 5-hydroxy-1,4-naphthoquinone.

(d) Reaction of 4-methyl-*N*-sulfinylaniline with 2-methyl-5-hydroxy-1,4-naphthoquinone (plumbagin)

In order to see the effect of a substituent in the 2-position in the cycloaddition we studied the reaction between plumbagin and 4-methyl-*N*-sulfinylaniline. The product isolated in this reaction (**5**) shows that 2 + 2 cycloaddition in the alkene



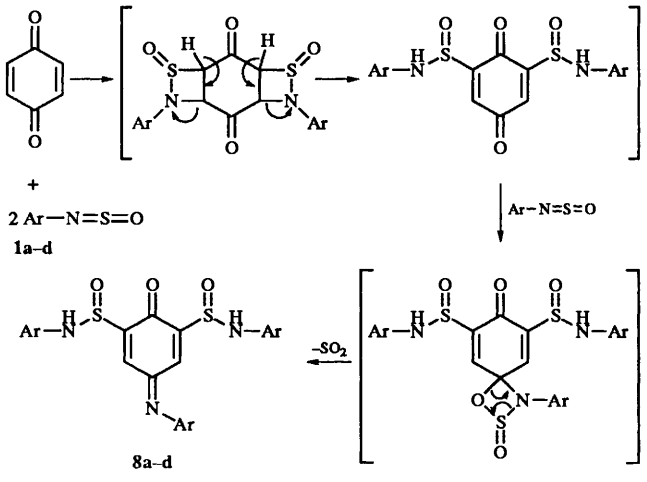
5 **6** **7**

fails when the 2-position is substituted with a methyl group, and the imine formation can be rationalised in terms of a 2 + 2 addition with one of the carbonyls followed by the elimination of SO_2 as in the case of reactions with 1,4-benzoquinone. The structure of the product was confirmed by NOE experiments. Irradiation of the one of the doublets of the *para*-substituted phenyl groups at δ 7.25 showed 5% NOE in the olefinic quartet at δ 7.12 and no enhancement was seen in the methyl doublet at δ 2.09. These results show that *N*-sulfinylamine reacts at the less hindered carbonyl group as expected.

(e) Reactions of *N*-sulfinylarylamines with 1,4-benzoquinone

Reactions of *N*-sulfinylarylamines with 1,4-benzoquinone were carried out using acetonitrile as the solvent because of the poor solubility of 1,4-benzoquinone in benzene. The reaction was first attempted using 1 equivalent of 4-methyl-*N*-sulfinylaniline at room temperature. The solution turned deep red after 2 days. The product was isolated in poor yield (9%) after preparative plate chromatography and was identified as **8d**. The product formed showed that three molecules of *N*-sulfinylamine have reacted with one molecule of 1,4-benzoquinone. Therefore, the reaction was repeated with 3 equivalents of 4-methyl-*N*-sulfinylaniline and leaving the mixture for 7 days. This reaction gave the same product **8d** in reasonably good yield. The adduct obtained from the reaction between 4-methyl-*N*-sulfinylaniline and 1,4-benzoquinone showed three methyl groups in the ^1H NMR spectrum, two overlapping at δ 2.36 and the third at δ 2.29. The ^{13}C spectrum also showed two signals corresponding to three methyl groups at δ 20.99 (two Me) and 20.82 (one Me). The two olefinic hydrogens of the quinone appear as singlets at δ 6.19 and 6.09 in the ^1H NMR and the corresponding carbon signals at δ 96.63 and 90.01 in the ^{13}C NMR spectrum. These values are comparable with the chemical shifts of similar hydrogens and carbons found in the 2-(*N*-arylsulfinamoyl)-1,4-naphthoquinone products. Further, two very broad signals were found at δ 8.64 and 7.60 in the ^1H NMR spectrum, which disappeared when the sample was treated with D_2O. These signals were assigned as two NH functions in different environments. Only one quinone carbonyl carbon signal was observed in the ^{13}C NMR spectrum. This signal was at δ 180.89, and this value is comparable with the carbonyl carbon chemical shifts of the 2-(*N*-arylsulfinamoyl)-1,4-naphthoquinones. The CI (CH_4) mass spectrum of this product gave the M + 1 peak at 504 showing the elimination of

a molecule of SO_2 during the formation of this product. This 3:1 adduct is the only product isolated from the reaction between 1,4-benzoquinone and *N*-sulfinylarylamine compounds. The structure **8d** was proposed for the adduct based on the spectral data. The asymmetry of the molecule arises as a result of the imine nitrogen. The difference in chemical shifts of the two olefinic protons (0.1 ppm) arises from this imine function at C-4. The third molecule of sulfinylamine reacts as expected at the less hindered carbonyl function as in the case of reaction with plumbagin. Three other *N*-sulfinylarylamines also gave similar adducts **8a–c** (Scheme 4). All attempts to isolate any intermediate products in this reaction were unsuccessful.



Scheme 4

The formation of this 3:1 adduct can be explained as follows. Two moles of *N*-sulfinylarylamine react with benzoquinone by a mechanism similar to the mechanism proposed for the reaction between *N*-sulfinylarylamines and 1,4-naphthoquinone. The third mole probably reacts *via* a 2 + 2 cycloaddition to one of the C=O groups in the quinone followed by the fragmentation elimination of SO_2. The exact order of this reaction sequence could not be determined as we have not been able to isolate or identify any intermediates. Therefore the order may be interchanged in the proposed mechanism shown.

(f) Hydrolysis of the *N*-sulfinylarylamine quinone compounds

Acid hydrolysis of the adduct 2-[*N*-(4-methylphenyl)sulfinamoyl]-1,4-naphthoquinone **2d** was attempted in 20% aqueous HCl and complete hydrolysis was seen after refluxing for 1 h. The product isolated after extraction was 2-hydroxy-1,4-naphthoquinone (lawsone) **6**. Acid hydrolysis of the sulfinamoyl function in cyclic systems has been reported by Hanson and Stone[5] and they have observed the protonation of the sulfinyl oxygen and cleavage of the N–S bond. Further, cleavage of the N–S bond during acid hydrolysis has been reported for cyclic 1,2-thiazine oxides as well, by Mock and Nugent.[18] Cleavage at C–S bond in the acid hydrolysis is a novel reaction. Protonation of the sulfinyl oxygen would make the sulfinamoyl group into a leaving group, allowing carbocation hydroxylation in this reaction. Therefore, *N*-sulfinylarylamine addition, followed by hydrolysis is an alternative method for the presently available methods[19] for the 2-hydroxylation of 1,4-naphthoquinone. Similar hydrolysis of the adduct **2f** also gave the same product, lawsone. Base hydrolysis of **2d** in refluxing 10% aqueous sodium hydroxide gave a complex mixture of intractable products.

Hydrolysis of the adducts obtained from the reactions between juglone and two *N*-sulfinylamines, **4a** and **4d** gave 2,8-dihydroxy-1,4-naphthoquinone[20] **7**. The identity of **7** was confirmed by comparison of the ^{13}C NMR data[20a] and mp,[20b] with the literature values. Therefore, this contribution is the first example of a regiospecific 3-hydroxylation of juglone. This methodology can be extended and applied to regioselective hydroxylations in alkenes in other substituted and more complex 1,4-naphthoquinone systems as well.

Acid hydrolysis of the adducts obtained from the reactions between 1,4-benzoquinone and *N*-sulfinylarylamines led to complex mixtures of products.

Experimental

Melting points were determined in open capillary tubes and are uncorrected. ^1H NMR spectra were recorded in a Bruker AC-F 200 spectrometer operating at 200.132 MHz in $CDCl_3$ or [$^2H_6$]DMSO solutions and chemical shifts are given in parts per million downfield from tetramethylsilane (δ = 0.00) or with reference to residual [$^2H_6$]DMSO signal at δ 2.49. *J* Values are given in Hz. ^{13}C NMR spectra in $CDCl_3$ solutions were recorded on the same spectrometer operating at 50.323 MHz. Chemical shifts were measured relative to $CDCl_3$ and converted to δ(TMS) values by using $\delta(CDCl_3)$ 77.00 or δ([$^2H_6$]DMSO) 39.50. Mass spectra were obtained in a Hewlett-Packard 5890 GC/MS in the EI mode or in the CI mode using CH_4 ionization. IR spectra were recorded on a JASCO 5300 FT-IR spectrometer or on a Perkin-Elmer 1420 spectrometer in $CHCl_3$ solutions. UV–VIS spectra were obtained using a JASCO V-560 spectrometer in MeOH solutions using 1 cm cells. All solvents were distilled before use. Preparative thin layer chromatography was carried out using BDH G6 silica gel coated on 20 × 20 cm glass plates. Column chromatography was carried out on Sigma 70–270 mesh silica.

Preparation of *N*-sulfinylarylamines 1a–h

N-Sulfinylarylamines were prepared according to the standard literature procedure.[1a] All *N*-sulfinylamines are known compounds,[3–5] except for *N*-sulfinyl-2-naphthylamine **1h** which was prepared in 92% yield, mp 101–105 °C (Found: C, 63.7; H, 3.6. $C_{10}H_7NOS$ requires C, 63.48; H, 3.73%); ν_{max}/cm^{-1} 3397, 3011, 1639, 1632, 1514, 1470, 1389, 1340, 1287, 1225, 1211, 1182, 1146, 843, 812, 783, 769, 750, 738, 733 and 619; $\delta_H(CDCl_3)$ 7.45–7.57 (2 H, m), 7.75–7.90 (4 H, m) and 8.43 (1 H, br s); $\delta_C(CDCl_3)$ 124.59, 126.98, 127.76, 128.01, 128.29, 128.99, 129.15, 132.99, 133.69 and 140.31.

Reactions of *N*-sulfinylarylamines 1a–h with 1,4-naphthoquinone

N-Sulfinylarylamine (2.00 mmol) was dissolved in dry benzene (5 cm^3) and 1,4-naphthoquinone (2.00 mmol) was added to it. The mixture was allowed to stand at room temperature in the dark, protected from moisture for 3 days. The solvent was evaporated under reduced pressure and the residue was purified by preparative plate chromatography using methylene chloride as the solvent.

2-(*N*-Phenylsulfinamoyl)-1,4-naphthoquinone 2a. Yield 62%, mp 186–189 °C (Found: C, 64.5; H, 3.8. $C_{16}H_{11}NO_3S$ requires C, 64.63; H, 3.73%); λ_{max}/nm 464 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 6508), 271 (34 245), 198 (37 034), 196 (35 717) and 192 (66 243); ν_{max}/cm^{-1} 3360 (NH), 1675 (C=O), 1614 (C=O), 1597, 1574, 1515, 1450, 1350, 1295 and 1124 (S=O) and 990; $\delta_H(CDCl_3)$ 6.43 (1 H, s, 3-H), 7.22 (1 H, dd, *J* 7.3, 8.0), 7.28 (2 H, d, *J* 9.0), 7.42 (2 H, dd, *J* 7.5, 8.3), 7.58 (1 H, br s, NH), 7.67 (1 H, dt, *J* 1.3, 7.7), 7.76 (1 H, dt, *J* 1.3, 7.7), 8.11 (1 H, dd, *J* 1.3, 7.5) and 8.13 (1 H, dd, *J* 1.3, 7.5); $\delta_C(CDCl_3)$ 103.35 (C-3), 122.59 (2 × C), 125.61, 126.15, 126.52, 129.68 (2 × C), 130.33, 132.35, 133.19, 134.92, 137.41, 144.69, 182.06 (C=O) and 183.95 (C=O); *m/z* (EI)

297 (4%), 249 (57), 220 (32), 204 (18), 193 (11), 165 (14), 144 (26), 104 (61) and 77 (100).

2-[*N*-(2-Methylphenyl)sulfinamoyl]-1,4-naphthoquinone 2b. Yield 48%, mp 153–155 °C (Found: C, 65.65; H, 4.2. $C_{17}H_{13}NO_3S$ requires C, 65.58; H, 4.21%); λ_{max}/nm 452 (ε/dm^3 mol^{-1} cm^{-1} 5971), 268 (32 032), 198 (53 274), 197 (56 166), 193 (67 456); ν_{max}/cm^{-1} 3364, 1674, 1614, 1600, 1574, 1502, 1349, 1292, 1217, 1215, 1212, 991, 762, 754, 719 and 672; δ_H($CDCl_3$) 2.27 (3 H, s, CH_3), 5.95 (1 H, s, 3-H), 7.21–7.30 (4 H, m), 7.33 (1 H, br s, NH), 7.67 (1 H, dt, *J* 1.3, 7.6), 7.76 (1 H, dt, *J* 1.3, 7.6), 8.10 (1 H, dd, *J* 1.3, 7.5) and 8.15 (1 H, dd, *J* 1.3, 7.5); δ_C($CDCl_3$) 17.62 (CH_3), 102.98 (C-3), 124.66, 126.05, 126.29, 126.75, 126.82, 127.02, 131.28, 132.14, 133.03, 133.25, 134.75, 135.34, 145.70, 181.99 (C=O) and 183.61 (C=O); *m*/*z* (CI) 312 (4%), 191 (72), 178 (2), 105 (30) and 77 (100).

2-[*N*-(3-Methylphenyl)sulfinamoyl]-1,4-naphthoquinone 2c. Yield 56%, mp 170–172 °C (Found: 65.7; H, 4.2. $C_{17}H_{13}NO_3S$ requires C, 65.58; H, 4.21%); λ_{max}/nm 459 (ε/dm^3 mol^{-1} cm^{-1} 2677), 272 (10 060), 208 (14 035), 203 (15 414) and 200 (17 930); ν_{max}/cm^{-1} 3359, 3010, 2360, 1674, 1605, 1574, 1526, 1493, 1350, 1331, 1292, 1245, 1222, 1218, 1214, 1210, 1120, 988, 787, 773, 761, 719 and 687; δ_H($CDCl_3$) 2.38 (3 H, s, CH_3), 6.42 (1 H, s, 3-H), 7.00–7.08 (2 H, m), 7.09 (1 H, br s), 7.29 (1 H, dt, *J* 1.5, 7.5), 7.56 (1 H, br s, NH), 7.65 (1 H, dt, *J* 1.3, 7.3), 7.75 (1 H, dt, *J* 1.3, 7.3), 8.09 (1 H, dd, *J* 1.3, 7.3) and 8.11 (1 H, dd, *J* 1.3, 7.3); δ_C($CDCl_3$) 21.39 (CH_3), 103.29 (C-5), 112.19, 115.86, 119.38, 119.57, 123.04, 126.39, 126.46, 129.42, 132.25, 134.84, 137.30, 139.71, 144.68, 182.03 (C=O) and 183.90 (C=O); *m*/*z* (EI) 263 (100%), 248 (35), 234 (23), 206 (12), 165 (8), 158 (16), 130 (11) and 91 (35).

2-[*N*-(4-Methylphenyl)sulfinamoyl]-1,4-naphthoquinone 2d. Yield 68%, mp 190–191 °C (Found: C, 65.5; H, 4.2. $C_{17}H_{13}NO_3S$ requires C, 65.58; H, 4.21%); λ_{max}/nm 468(ε/dm^3 mol^{-1} cm^{-1} 4087), 271 (21 415), 206 (26 035), 202 (27 723) and 200 (29 056); ν_{max}/cm^{-1} 3350, 2360, 1603, 1215, 786, 732, 720 and 667; δ_H($CDCl_3$) 2.36 (3 H, s, CH_3), 6.35 (1 H, s, 3-H), 7.15 (2 H, d, *J* 8.6), 7.21 (2 H, d, *J* 8.6), 7.54 (1 H, br s, NH), 7.65 (1 H, dt, *J* 1.2, 7.6), 7.75 (1 H, dt, *J* 1.2, 7.6), 8.09 (1 H, dd, *J* 1.4, 7.6) and 8.10 (1 H, dd, *J* 1.4, 7.6); δ_C($CDCl_3$) 20.92 (CH_3), 102.9 (C-3), 122.66 (2 × C), 126.08, 126.42, 130.17 (2 × C), 130.31, 132.20, 133.24, 134.66, 134.84, 135.56, 144.95, 183.01 (C=O) and 183.82 (C=O); *m*/*z* (CI) 312 (37%), 191 (100), 178 (11), 152 (5), 122 (4), 105 (34) and 77 (29).

2-[*N*-(3-Chlorophenyl)sulfinamoyl]-1,4-naphthoquinone 2e. Yield 21%, mp 220–222 °C (Found: C, 57.75; H, 3.0. $C_{16}H_{10}ClNO_3S$ requires C, 57.92; H, 3.04%); λ_{max}/nm 457 (ε/dm^3 mol^{-1} cm^{-1} 7060), 272 (32 022), 208 (26 752), 200 (8851), 199 (23 072); ν_{max}/cm^{-1} 3013, 2358, 1615, 1592, 1520, 1347, 1215, 1212, 1209, 922, 771 and 757; δ_H($CDCl_3$) 6.43 (1 H, s, 3-H), 7.18 (2 H, m), 7.29 (1 H, m), 7.36 (1 H, t, *J* 8.0), 7.55 (1 H, br s, NH), 7.68 (1 H, dt, *J* 1.3, 7.3), 7.78 (1 H, dt, *J* 1.3, 7.3), 8.11 (1 H, dd, *J* 1.3, 73) and 8.13 (1 H, dd, *J* 1.3, 7.3); δ_C($CDCl_3$) 104.22 (C-3), 120.49, 122.43, 125.59, 126.24, 126.63, 130.24, 130.78, 132.55, 133.03, 135.04, 135.39, 138.78, 144.17, 181.77 (C=O) and 183.00 (C=O).

2-[*N*-(4-Chlorophenyl)sulfinamoyl]-1,4-naphthoquinone 2f. Yield 27%, mp 248–250 °C (Found: C, 56.0; H, 3.3. $C_{16}H_{10}ClNO_3S$ requires C, 57.92; H, 3.04%); λ_{max}/nm 461 (ε/dm^3 mol^{-1} cm^{-1} 2121), 271 (7293), 209 (3049), 199 (12 729) and 198 (11 492); ν_{max}/cm^{-1} 3013, 2341, 2049, 1635, 1297, 1224, 1215, 1211, 1209, 794, 784 and 770; δ_H($CDCl_3$) 6.36 (1 H, s, 3-H), 7.72 (2 H, d, *J* 8.6), 7.40 (2 H, d, *J* 8.6), 7.52 (1 H br, s, NH), 7.71 (1 H, dt, *J* 1.3, 7.3), 7.78 (1 H, dt, *J* 1.3, 7.3), 8.11 (1 H, dd, *J* 1.3, 7.3), 8.14 (dd, *J* 7.3); *m*/*z* (EI) 331 (25%), 296 (43), 273 (49), 246 (21), 217 (24), 190 (29), 172 (15), 158 (15), 137 (33), 91 (16) and 77 (100).

2-[*N*-(3-Nitrophenyl)sulfinamoyl]-1,4-naphthoquinone 2g. Yield 44%, mp 112–114 °C (Found: C, 56.0; H, 2.75. $C_{16}H_{10}N_2O_5S$ requires C, 57.14; H, 2.85); λ_{max}/nm 253 (ε/dm^3 mol^{-1} cm^{-1} 9952), 224 (8208), 219 (9029), 210 (23 803) and 209 (21 443); ν_{max}/cm^{-1} 3026, 2361, 1606, 1535, 1352, 1213, 792, 783, 777, 769, 752 and 733; δ_H($CDCl_3$) 6.48 (1 H, s, 3-H), 6.95 (1 H, dd, *J* 2.5, 7.5), 7.28 (1 H, t, *J* 8.0), 7.59 (1 H, t, *J* 2.5), 7.55–7.85 (4 H, m) and 8.15 (2 H, m); *m*/*z* (EI) 235 (3%), 217 (3), 161 (10), 145 (18), 131 (2), 117 (4), 89 (45) and 73 (100).

2-[*N*-(2-Naphthyl)sulfinamoyl]-1,4-naphthoquinone 2h. Yield 72%, mp 95–97 °C (Found: C, 69.3; H, 3.8. $C_{20}H_{13}NO_3S$ requires C, 69.15; H, 3.78%); λ_{max}/nm 235 (ε/dm^3 mol^{-1} cm^{-1} 31 682), 206 (58 024), 203 (50 782), 200 (39 648) and 198 (78 663); ν_{max}/cm^{-1} 3567, 1634, 1576, 1302, 1184, 991, 832, 792, 775 and 723; δ_H($CDCl_3$) 6.57 (1 H, s, 3-H), 6.80–6.95 (1 H, m), 6.95 (1 H, br s, NH), 7.21 (1 H, dt, *J* 1.3, 7.2), 7.35 (1 H, dt, *J* 1.3, 7.2), 7.40–7.87 (6 H, m), 8.11 (1 H, d, *J* 7.2), 8.12 (1 H, d, *J* 7.2); δ_C($CDCl_3$) 103.61 (C-3), 108.51, 118.16, 122.31, 125.73, 126.12, 126.51, 127.02, 127.43, 127.72, 129.13, 129.66, 130.29, 132.33, 133.16, 134.89, 144.05, 181.96 (C=O) and 183.97 (C=O).

Reaction of 1,4-bis(*N*-sulfinylamino)benzene with 1,4-naphthoquinone

1,4-Bis(*N*-sulfinylamino)benzene (2 mmol) was dissolved in dry benzene (5 cm^3) and 1,4-naphthoquinone (4 mmol) was added to it and the resulting mixture was kept in the dark, protected from moisture for 6 days. The product 2-[*N*-(4-aminophenyl)-sulfinamoyl]-1,4-naphthoquinone **3** (412 mg, 66%) was isolated by column chromatography on silica gel eluting with 2% methanol in methylene dichloride. Unchanged 1,4-naphthoquinone (237 mg, 1.5 mmol) was recovered during the chromatography.

Data for compound **3**: mp 219–220 °C (Found: C, 61.6; H, 3.9. $C_{16}H_{12}N_2O_3S$ requires C, 61.53; H, 3.88%); λ_{max}/nm 502 (ε/dm^3 mol^{-1} cm^{-1} 4591), 374 (2436), 224 (25 995), 203 (28 625) and 197 (25 861); ν_{max}/cm^{-1} 3736, 3567, 1606, 1521, 1222, 1219, 1120, 990 and 789; δ_H($CDCl_3$) 3.70 (2 H, br s, NH_2), 6.20 (1 H, s, 3-H), 6.72 (2 H, d, *J* 8.0), 7.06 (2 H, d, *J* 8.0), 7.41 (1 H, br s, NH), 7.64 (1 H, dd, *J* 7.2, 7.2) and 8.10 (2 H, d, *J* 7.2); δ_C($CDCl_3$) 102.20 (C-3), 115.76, 124.88, 126.10, 126.39, 127.91, 130.44, 132.09, 134.49, 144.75, 145.80, 182.28 (C=O) and 183.66 (C=O).

Reactions of *N*-sulfinylarylamines with 5-hydroxy-1,4-naphthoquinone (juglone)

Two of the *N*-sulfinylarylamines **1a** and **1d** were treated with 5-hydroxy-1,4-naphthoquinone, using the same procedure as in the case of 1,4-naphthoquinone, compounds **4a** and **4d**, respectively were isolated. 8-Hydroxy-2-(*N*-phenylsulfinamoyl)-1,4-naphthoquinone **4a** (76%), mp 236–237 °C (Found: C, 61.4; H, 3.4. $C_{16}H_{11}NO_4S$ requires C, 61.33; H, 3.53%); λ_{max}/nm 660 (ε/dm^3 mol^{-1} cm^{-1} 329), 648 (376), 413 (7990), 271 (27 212) and 204 (32 570); ν_{max}/cm^{-1} 3118, 1592, 1507, 1222, 1218 and 794; δ_H($CDCl_3$) 6.37 (1 H, s, 3-H), 7.19 (1 H, dd, *J* 3.5, 6.0), 7.27 (3 H, m), 7.43 (2 H, dd, *J* 7.0, 8.0), 7.54 (1 H, br s, NH), 7.64 (1 H, d, *J* 3.5), 7.65 (1 H, d, *J* 6.0), 11.57 (1 H, s, OH); δ_C($CDCl_3$) 103.88 (C-3), 113.97, 118.76, 122.63, 122.77 (2 × C), 125.84, 129.73 (2 × C), 133.06, 137.84, 144.65, 161.72, 183.13 (C=O) and 186.13 (C=O); *m*/*z* (EI) 265 (100%, M^+ − SO), 220 (24), 180 (6), 144 (15), 120 (18), 77 (43) and 51 (24).

8-Hydroxy-2-[*N*-(4-methylphenyl)sulfinamoyl]-1,4-naphthoquinone **4d** (70%), mp 189–190 °C (Found: C, 62.5; H, 4.1. $C_{17}H_{13}NO_4S$ requires C, 62.37; H, 4.01%); λ_{max}/nm 660 (ε/dm^3 mol^{-1} cm^{-1} 442), 412 (7368), 271 (25 397), 225 (16 899) and 204 (32 619); ν_{max}/cm^{-1} 3688, 3365, 1632, 1597, 1575, 1456, 1374, 1316, 1275, 1230, 935 and 827; δ_H($CDCl_3$) 2.38 (3 H, s, CH_3), 6.30 (1 H, s, 3-H), 7.14 (2 H, d, *J* 8.0), 7.20 (1 H, m), 7.23 (2 H, d, *J* 8.0), 7.49 (1 H, br s, NH), 7.62 (1 H, d, *J* 3.5), 7.63 (1

H, d, J 6.0) and 11.56 (1 H, s, OH); $\delta_C(CDCl_3)$ 20.97 (CH_3), 103.49 (C_3), 113.97, 118.70, 122.50, 122.83 (2 × C), 130.25 (2 × C), 133.15, 134.44, 135.85, 137.78, 144.90, 161.68, 183.01 (C=O) and 186.18 (C=O); m/z (EI) 279 (100%, $M^+ - SO$), 264 (33), 234 (16), 207 (3), 158 (11), 131 (10), 120 (16), 91 (19) and 65 (18).

Reaction of 4-methyl-*N*-sulfinylaniline with 5-hydroxy-2-methyl-1,4-naphthoquinone (plumbagin)

4-Methyl-*N*-sulfinylaniline (0.2 mmol) was treated with 5-hydroxy-2-methyl-1,4-naphthoquinone (0.2 mmol) using the same procedure as in the case of 1,4-naphthoquinone. The product was isolated by column chromatography on silica gel eluting with methylene dichloride, and identified as 5-hydroxy-2-methyl-4-(4-methylphenyl)imino-1,4-dihydronaphthalen-1-one **5** (87%), mp 67–69 °C (decomp.) (Found: C, 77.9; H, 5.6. $C_{18}H_{15}NO_2$ requires C, 77.96; H, 5.45%); λ_{max}/nm 656 (ε/dm^3 mol^{-1} cm^{-1} 1871), 401 (2287), 282 (8111) and 203 (24 704); ν_{max}/cm^{-1} 3325, 3009, 2925, 1622, 1545, 1516, 1457, 1268, 1218, 1211, 1017, 816 and 788; $\delta_H(CDCl_3)$ 2.09 (3 H, d, J 1.5, 2-CH_3), 2.42 (3 H, s, Ar-CH_3), 6.93 (2 H, d, J 8.0), 7.12 (1 H, q, J 1.5), 7.20 (2 H, d, J 8.0), 7.28 (1 H, dd, J 1.5, 8.0), 7.51 (1 H, dd, J 8.0, 8.0) and 7.72 (1 H, dd, J 1.5, 8.0); $\delta_C(CDCl_3)$ 16.75, 20.46, 118.36, 120.88, 123.29, 126.92, 128.79, 129.73, 131.63, 132.65, 136.02, 143.20, 144.31, 159.76, 160.62 and 185.40 (C=O).

Acid hydrolysis of arylsulfinamoyl-1,4-naphthoquinones

Arylsulfinamoyl-1,4-naphthoquinone (1.00 mmol) was suspended in 20% aqueous hydrochloric acid (5 cm^3) and refluxed for 1.0 h. The reaction mixture was allowed to cool and diluted with water (10 cm^3) and extracted with chloroform (3 × 10 cm^3). The combined chloroform layers were washed with water (10 cm^3) and dried with anhydrous Na_2SO_4. Evaporation of the solvents, and chromatography on silica gel eluting with methylene dichloride–methanol (9 : 1) gave the pure product.

Hydrolysis of the adduct **2a** gave 2-hydroxy-1,4-naphthoquinone **6** (90%), mp 194–195 °C (lit.,[19a] 195–196 °C); δ_H ([$^2H_6$]DMSO) 5.57 (1 H, s, 3-H), 7.59 (1 H, dd, J 7.0, 7.0), 7.71 (1 H, dd, J 7.0, 7.0), 7.84 (2 H, d, J 7.0) and 11.22 (1 H, s, OH); δ_C([$^2H_6$]DMSO) 107.85 (C-3), 125.68 (2 × C), 131.44 (2 × C), 135.21 (2 × C), 170.88 (C-2), 182.93 (C=O) and 187.70 (C=O); m/z (EI) 174 (M^+, 77%), 146 (19), 105 (100) and 51 (21). Hydrolysis of the adduct **2d** also gave 2-hydroxy-1,4-naphthoquinone **6** (86%).

Hydrolysis of the adduct **4a** gave 2,8-dihydroxy-1,4-naphthoquinone **7** (88%), mp 210–215 °C (lit.,[20b] 218–220 °C); δ_H([$^2H_6$]DMSO) 6.03 (1 H, s, 3-H), 7.13 (1 H, dd, J 1.0, 8.0), 7.34 (1 H, dd, J 1.0, 7.2), 7.59 (1 H, dd, J 7.2, 8.0) and 11.53 (1 H, s); δ_C([$^2H_6$]DMSO) 109.63 (C-3), 112.48, 116.68, 121.80, 130.63, 135.98, 158.59, 159.11, 183.04 and 184.40; m/z (EI) 190 (100%, M^+), 162 (27, $M^+ - CO$), 144 (3, $M^+ - CO - H_2O$), 134 (16, $M^+ - 2 \times CO$), 121 (48), 120 (47), 92 (24), 77 (11), 63 (25) and 51 (13). Hydrolysis of the adduct **4d** also gave 2,8-dihydroxy-1,4-naphthoquinone **7** (82%).

Reactions of *N*-sulfinylarylamines 1a–d with 1,4-benzoquinone

N-Sulfinylarylamine (6.00 mmol) was dissolved in dry acetonitrile (10 cm^3) and 1,4-benzoquinone (2.00 mmol) was added to it. The mixture was allowed to stand at room temperature in the dark, protected from moisture for 7 days. The solvent was evaporated under reduced pressure and the residue was purified by preparative plate chromatography using methylene dichloride as the solvent.

4-Phenylimino-2,5-bis(*N*-phenylsulfinamoyl)cyclohexa-2,5-dien-1-one. 8a. Yield 45%, mp 197–199 °C (Found: C, 62.5; H, 4.12. $C_{24}H_{19}N_3O_3S_2$ requires C, 62.46; H, 4.15%); λ_{max}/nm 379 (ε/dm^3 mol^{-1} cm^{-1} 7744), 252 (130 046), 210 (15 490), 197 (14 983) and 192 (19 362); ν_{max}/cm^{-1} 3693, 3016, 1604, 1582, 1551, 1511, 1344, 1296, 1265, 1220, 1214, 1212, 1176, 909, 845, 795, 765, 720 and 651; $\delta_H(CDCl_3)$ 6.17 (1 H, s), 6.19 (1 H, s), 6.95 (4 H, d, J 8.0), 7.05 (4 H, d, J 8.0), 7.12–7.45 (7 H, m), 7.65 (1 H, br s) and 8.67 (1 H, br s); $\delta_C(CDCl_3)$ 90.50, 97.08, 120.79, 120.91, 123.05, 123.96, 124.72, 125.43, 128.96, 129.37, 129.53, 137.96, 138.62, 140.64, 149.29, 149.55, 153.85 and 181.04 (C=O).

2,5-Bis[*N*-(2-methylphenyl)sulfinamoyl]-4-phenyliminocyclohexa-2,5-dien-1-one 8b. Yield 53%, mp 110–114 °C (Found: C, 64.3; H, 5.0. $C_{27}H_{25}N_3O_3S_2$ requires C, 64.39; H, 5.00%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1} 12 554), 212 (45 028), 210 (44 907), 205 (40 561) and 200 (48 650); ν_{max}/cm^{-1} 3336, 3011, 1577, 1508, 1460, 1340, 1289, 1219, 1212, 1209, 1177 and 909; $\delta_H(CDCl_3)$ 2.17 (3 H, s, CH_3), 2.23 (3 H, s, CH_3), 2.32 (3 H, s, CH_3), 5.78 (1 H, s), 5.84 (1 H, s), 6.68 (1 H, d, J 8.0), 6.77 (1 H, d, J 7.5) and 6.97–7.45 (12 H, m); $\delta_C(CDCl_3)$ 17.73 (CH_3), 17.79 (CH_3), 18.06 (CH_3), 89.78, 96.48, 114.87, 118.58, 119.41, 121.92, 124.61, 124.80, 126.02, 126.29, 126.58, 126.90, 129.52, 130.49, 131.07, 131.19, 131.29, 132.89, 136.68, 141.48, 147.83, 150.38 and 180.97 (C=O); m/z (CI) 504 (1%), 435 (4), 379 (7), 317 (2), 277 (44), 219 (47), 170 (25), 125 (8) and 97 (100).

2,5-Bis[*N*-(3-methylphenyl)sulfinamoyl]-4-phenyliminocyclohexa-2,5-dien-1-one 8c. Yield 47%, mp 75–77 °C (Found: C, 64.4; H, 5.0%. $C_{27}H_{25}N_3O_3S_2$ requires C, 64.39; H, 5.00%); λ_{max}/nm 384 (ε/dm^3 mol^{-1} cm^{-1} 13 762), 248 (23 057), 207 (39 354), 203 (36 819) and 201 (39 958); ν_{max}/cm^{-1} 3368, 3009, 1578, 1516, 1340, 1292, 1265, 1222, 1220, 1218, 1212, 1208, 1170, 785, 782, 776, 773, 772, 767 and 763; $\delta_H(CDCl_3)$ 2.26 (3 H, s, CH_3), 2.37 (6 H, s, 2 × CH_3), 6.16 (1 H, s), 6.19 (1 H, s), 6.48 (2 H, d, J 7.5), 6.57 (2 H, d, J 7.5), 6.72–7.15 (7 H, m) and 7.21–7.33 (3 H, m); $\delta_C(CDCl_3)$ 21.39 (3 × CH_3), 90.81, 97.02, 112.20, 115.86, 117.83, 117.99, 119.40, 119.93, 121.20, 121.57, 123.44, 124.59, 125.38, 126.13, 128.65, 129.10, 129.25, 137.84, 138.71, 139.17, 139.47, 149.43, 153.82 and 181.07 (C=O); m/z (CI) 504 (1%), 463 (1), 425 (9), 407 (4), 338 (22), 219 (32), 175 (28), 125 (100).

2,5-Bis[*N*-(4-methylphenyl)sulfinamoyl]-4-phenyliminocyclohexa-2,5-dien-1-one 8d. Yield 57%, mp 188–190 °C (Found: C, 64.4; H, 5.05. $C_{27}H_{25}N_3O_3S_2$ requires C, 64.39; H, 5.00%); λ_{max}/nm 390 (ε/dm^3 mol^{-1} cm^{-1} 14 815), 273 (16 919), 205 (20 760), 203 (18 839), 202 (19 388); ν_{max}/cm^{-1} 3610, 3019, 2926, 2342, 1734, 1653, 1578, 1518, 1499, 1341, 1299, 1222, 1217, 1211, 1209, 1173, 1017, 816, 791, 770, 737 and 677; $\delta_H(CDCl_3)$ 2.29 (3 H, s, CH_3), 2.36 (6 H, s, 2 × CH_3), 6.09 (1 H, s), 6.19 (1 H, s), 6.87 (2 H, d, J 7.8), 6.96 (2 H, d, J 7.8), 7.09 (2 H, J, 7.8), 7.18 (2 H, d, J 7.8), 7.20 (4 H, br s), 7.60 (1 H, br s) and 8.64 (1 H, br s); $\delta_C(CDCl_3)$ 20.82 (CH_3), 20.99 (2 × CH_3), 90.01, 96.63, 120.79, 121.15, 123.12, 129.91, 130.03, 133.64, 134.37, 135.27, 135.31, 136.07, 140.83, 146.55, 150.02, 153.44 and 180.9 (C=O); m/z (CI) 504 (1%), 453 (1), 425 (15), 307 (1), 279 (7), 219 (6), 205 (75) and 149 (100).

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