

## Thermal Reactivity of 4'-Substituted- and 4'-Substituted-2-phenyl-benzenesulphenanilides

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The thermal decomposition of 4'-nitro-, 4'-H-, and 4'-methoxy-benzenesulphenanilides in benzene and/or furan, and of 4'-substituted-2-phenylbenzenesulphenanilides (**1d–f**) in benzene, was found to proceed by two distinct pathways: (i) nucleophilic displacement by furan and/or another sulphenanilide unit and (ii) homolytic S–N bond fission to give sulphenyl and anilino radicals. An increase in the electron-withdrawing capability of the 4'-substituent favours the ionic pathway, whereas the radical pathway is favoured by an increase in the reaction temperature.

Thermolysis of arenesulphenanilides has been reported<sup>1–4</sup> to effect homolysis of the S–N bond and to lead to products arising from hydrogen abstraction and/or dimerisation of the resulting anilino and sulphenyl radicals and to rearrangement products [*i.e.* to *o*- and *p*-(aryltio)anilines], which are believed to be formed by recombination of these radicals in a solvent cage. The arenesulphenanilide rearrangement has been shown to be acid-catalysed.<sup>3a,b</sup> More recently, the thermal rearrangement of *N*-methylalkanesulphenanilides has been suggested to occur *via* an intermolecular route.<sup>5</sup>

Previously we have reported the acid-promoted reaction of a number of benzenesulphenanilides at room temperature both in the absence<sup>6a</sup> and in the presence of alkenes.<sup>6b,c</sup> Now we report the results of our study on the thermal reactions of the 4'-substituted- and 4'-substituted-2-phenyl-benzenesulphenanilides (**1a–f**), carried out at 85 and 150 °C. This study was undertaken in order to investigate the effects of 4'-substituents and temperature on the thermal reactivity of these compounds. Although considerable attention has so far been devoted to the thermal reactions of sulphenanilides, the possible influence of *N*-aryl substituents and temperature is largely unknown.

### Results and Discussion

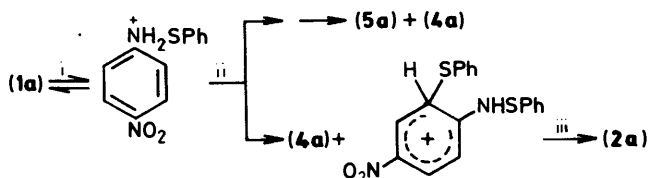
The thermal decomposition of 4'-nitrobenzenesulphenanilide (**1a**) (0.2M in benzene), carried out at 85 °C for 120 h, led after column chromatography to the isolation of 4'-nitro-2-(phenylthio)benzenesulphenanilide (**2a**) and 4-nitro-2-(phenylthio)aniline (**3a**) in addition to 4-nitroaniline (**4a**), diphenyl disulphide (**5a**) and unchanged starting material (**1a**) (Table 1).

When the same reaction was followed by t.l.c., compounds (**2a**) and (**4a**) were found to be the only detectable products in the initial stages of the reaction; progressive occurrence of the rearrangement product (**3a**) was observed subsequently, but the extent of the sulphenylated anilide (**2a**) remained roughly constant. Moreover, a control experiment showed that under the same conditions the anilide (**2a**) gave mainly the aniline (**3a**) and the disulphide (**5a**), as evidenced by t.l.c. These findings suggest that the sulphenylated anilide (**2a**) should be responsible for the formation of the aniline (**3a**). The anilide (**2a**) would result from electrophilic sulphenylation of compound (**1a**) by another sulphenanilide unit, since specific attack at the activated position *ortho* to the NHSPh group is consistent with electrophilic attack. On the other hand, homolytic substitution of compound (**1a**) by phenylthio radicals which may be formed would be unlikely in view of the known, scarce reactivity of arylthio radicals towards aromatic substrates.<sup>7</sup> This view is supported by our trapping experiments with furan and cyclohexene. The anilide (**1a**) in furan gave 2-(phenylthio)furan (**6**) in fair yield, as expected for electrophilic substitution;<sup>7c,8</sup> a

marked reduction in the yields of the aniline (**3a**) and the disulphide (**5a**) [and no anilide (**2a**)] was concomitantly observed (Table 1). Heating compound (**1a**) in benzene containing a five-fold excess of cyclohexene (1M) gave the *trans*-arylamino sulphide (**7**), the same product as previously obtained from the BF<sub>3</sub>-promoted electrophilic addition of compound (**1a**) to cyclohexene,<sup>6b,c</sup> together with minor amounts of the *trans*-adduct (**8**) and small amounts of a compound which was probably the arylaminocyclohexene (**9**) (4%). Again, a strong decrease in the yield of the disulphide (**5a**) and, particularly, essentially no production of compounds (**2a**) and (**3a**) were observed (Table 1). The adduct (**8**) probably results from sulphenylation of the first formed adduct (**7**), as supported by control experiments which showed that compound (**7**) was initially formed as a major product exclusive of the bis-sulphide (**8**), and that it reacted with the anilide (**1a**) under analogous conditions to give compound (**8**).

On this basis, it might be inferred that in the presence of a five-fold excess of cyclohexene the anilide (**1a**) would mainly give electrophilic addition to the alkene and sulphenylation of the resulting adduct. However, our subsequent observation that the anilide (**1a**) remained virtually unchanged upon heating at 85 °C in cyclohexene, acetonitrile, or 1M-cyclohexene in acetonitrile rules out the possibility that compound (**1a**) is itself the electrophile involved in the above thermal reactions.

We assume that the conjugate acid of the anilide (**1a**) is the actual electrophilic species. This might be in thermal protic equilibrium with the anilide (**1a**) possibly as the result of autoprotolysis. The protonated anilide (**1a**) would be expected<sup>6</sup> to be capable of undergoing nucleophilic attack at the activated S–N bond by an active aromatic ring, ultimately leading to aromatic sulphenylation with displacement of 4-nitroaniline (**4a**), and by alkene eventually leading to *trans*-addition. Furthermore, the protonated anilide (**1a**) would be expected to afford the disulphide (**5a**) and the aniline (**4a**) presumably by some reaction with another sulphenanilide unit<sup>6a</sup> (Scheme 1).



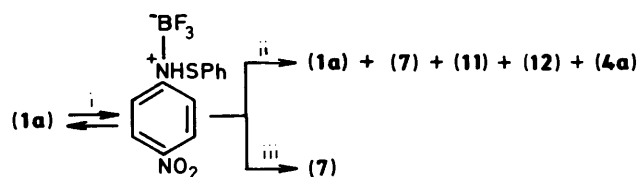
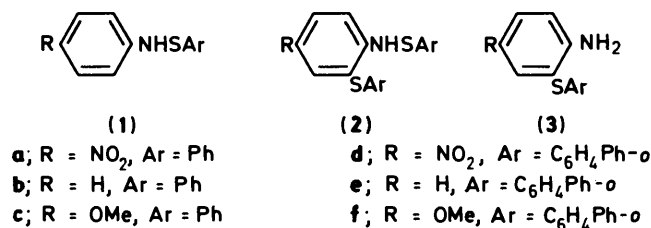
Scheme 1. Reagents: i, H<sup>+</sup>; ii, + (**1a**); iii, –H<sup>+</sup>

Our assumption is supported by the findings that in the presence of catalytic amounts of triethylamine (TEA) the decomposition of anilide (**1a**) was totally suppressed in benzene and furan, whereas the addition of trifluoroacetic acid (TFA)

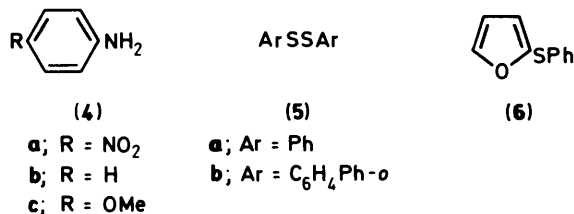
**Table 1.** Yields (%) of products from the thermal decomposition of 4'-nitrobenzenesulphenanilide (**1a**) (0.2M)

Conditions	Time (h)	Conversion (%)	(Phenylthio)-sulphenanilide ( <b>2a</b> ) <sup>a</sup>	(Phenylthio)-aniline ( <b>3a</b> ) <sup>b</sup>	Aniline ( <b>4a</b> ) <sup>b</sup>	Diphenyl disulphide ( <b>5a</b> ) <sup>a</sup>	(Phenylthio)-furan ( <b>6</b> ) <sup>b</sup>	Amino-sulphide ( <b>7</b> ) <sup>b</sup>	Amino-sulphide ( <b>8</b> ) <sup>a</sup>
Benzene, 85 °C	120	74	9	27	44	43			
Benzene, 85 °C <sup>c</sup>	120	0							
Benzene, 150 °C	15	100		24	30	60			
Furan, 85 °C	120	86		9	77	10	45		
Furan, 85 °C <sup>a</sup>	120	0							
Furan, 150 °C	15	100		8	56	36	22		
Furan, 150 °C <sup>c</sup>	15	100			70	65			
1M-Cyclohexene in benzene, 85 °C	120	100		3	41	23		34	20
Cyclohexene, 85 °C	120	0			78	82		4	
Cyclohexene, 150 °C	15	100							

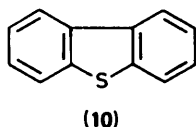
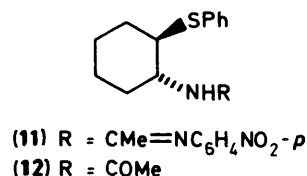
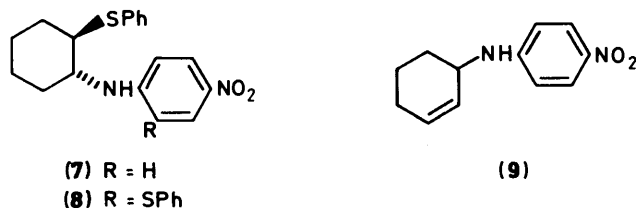
<sup>a</sup> Isolated yields based on 2 mol of (**1a**) reacting to give 1 mol of each of the products. <sup>b</sup> Isolated yields based on 1 mol of (**1a**) reacting to give 1 mol of each of the products. <sup>c</sup> In the presence of triethylamine ( $3.3 \times 10^{-2}$  equiv.).



**Scheme 2.** Reagents: and conditions: i, BF<sub>3</sub>·Et<sub>2</sub>O; ii, 1M-cyclohexene in acetonitrile, 85 °C, 24 h; iii, cyclohexene, 85 °C, 12 h



ion arising from electrophilic attack of the BF<sub>3</sub>-anilide (**1a**) complex to the alkene<sup>6b,c</sup> would be effectively trapped by the nitrile solvent to give ultimately the amidino sulphide (**11**) and the acetamido sulphide (**12**) upon aqueous work-up of the reaction mixture, as expected.<sup>10</sup> Thus, the failure of the anilide (**1a**) to undergo any reaction either in cyclohexene or in acetonitrile would result from a lack of acid catalysis, but the actual reasons are unclear.



(0.2 equiv.) enhanced the decomposition rate of anilide (**1a**) in benzene, without leading to any substantial change in the product pattern (see Experimental section).

Further support comes from the reactions in cyclohexene and 1M-cyclohexene in acetonitrile, carried out in the presence of boron trifluoride-diethyl ether (0.1 equiv.). In cyclohexene, the anilide (**1a**) was totally decomposed within 12 h to give the adduct (**7**) as the only product detectable by t.l.c., whereas in cyclohexene-acetonitrile, after 24 h, it gave the *trans* adducts (**7**), (**11**), and (**12**) (25, 35, and 30% respectively) in addition to 4-nitroaniline (**4a**) (33%) and unchanged starting material (40%)<sup>9</sup> (Scheme 2). In this latter case, the intermediate episulphonium

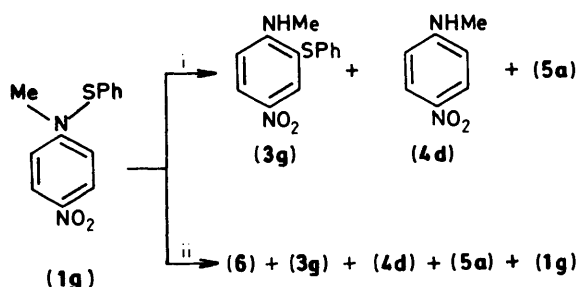
We have also investigated the thermal chemical behaviour of *N*-methyl-4'-nitrobenzenesulphenanilide (**1g**) in order to explore the effect of *N*-methyl substitution, which would prevent the possible autoprotolysis of anilide (**1a**). Heating the anilide (**1g**) in benzene at 85 °C for 6 days led to the separation of the rearrangement product (**3g**) (83%) in addition to *N*-methyl-4-nitroaniline (**4d**) (15%) and the disulphide (**5a**) (14%) (Scheme 3). No sulphenylated anilide analogue of compound (**2a**) was obtained. No evidence for any possible intermediacy of such a compound could be obtained when the reaction was followed by t.l.c. The disulphide (**5a**) and the aniline (**4d**) were the only detectable products in the initial stages of the reaction, progressive formation of the rearrangement product (**3g**) being observed subsequently. Under the same conditions, the anilide (**1g**) in furan gave 2-(phenylthio)furan (**6**) (40%) and the aniline (**3g**) (4%) along with *N*-methyl-4-nitroaniline (**4d**) (79%), the disulphide (**5a**) (25%), and unchanged starting material (**1g**) (76%) (Scheme 3). Moreover, the anilide (**1g**) was found to remain largely unchanged upon heating at 85 °C in benzene containing a five-fold excess of cyclohexene, in which case only

**Table 2.** Yields (%) of products from thermal decomposition of 4'-R-biphenyl-2-sulphenanilides (**1d-f**) (0.2M in benzene)

R	T (°C), t (h)	Conversion (%)	Disulphide (5b) <sup>a</sup>	Aniline <sup>b</sup> (4)	(Biphenylthio)sulphenanilide <sup>a</sup> (2d)	(Biphenylthio)aniline <sup>b</sup> (3d)	Dibenzothiophene (10) <sup>b</sup>	Phenazine (14) <sup>a</sup>	Azo-compound (15) <sup>a</sup>
NO <sub>2</sub>	85, 240	74	57	52 (4a)	10 (2d)	12 (3d)	trace 17		
	150, 20	100	50	68 (4a)		20 (3d)			
	150, 20 <sup>c</sup>	94	75	60 (4a)					
H	85, 480	50	75	25 (4b)	18 (16)	6 (3e)			
	85, 480 <sup>c</sup>	6	1	1 (4b)					
	150, 40	96	79	27 (4b)	10 <sup>d</sup>				
	150, 40 <sup>c</sup>	91	80	28 (4b)	4 <sup>d</sup>				
OMe	85, 720	70	81	29 (4c)	6 (2f)		12	12	
	150, 40	96	91	17 (4c)		3 (3f)	26	12	

<sup>a</sup> Isolated yields based on 2 mol of (1) reacting to give 1 mol of each of the products. <sup>b</sup> Isolated yields based on 1 mol of (1) reacting to give 1 mol of each of the products. <sup>c</sup> In the presence of triethylamine ( $3.3 \times 10^{-2}$  equiv.). <sup>d</sup> Unresolved mixture of the isomeric anilines (3e) and (13b).

small amounts of the disulphide (**5a**) and the anilide (**4d**) were detected by t.l.c. after a comparable time. Similar results were obtained in acetonitrile.



**Scheme 3.** Reagents and conditions: i, benzene, 85 °C, 6 days; ii, furan, 85 °C, 6 days

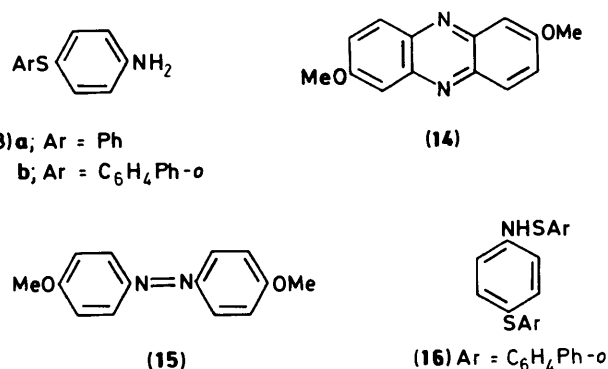
Thus, it appears that the anilide (**1g**) leads to the rearrangement product (**3g**) by way of an ionic, intermolecular route; this might be acid-catalysed by the aniline (**4d**) initially formed by homolytic degradation of anilide (**1g**). Nucleophilic displacement at the sulphur of protonated anilide (**1g**) by the aniline (**4d**) would lead to the sulphide (**3g**) with regeneration of the aniline reactant. A similar mechanism has been previously suggested for related rearrangements of *N*-methylalkane-sulphenanilides.<sup>5</sup>

However, it is unclear why no sulphenylation of the methylated anilide (**1g**) would occur, although steric hindrance due to the *N*-methyl substituent might play a determining role.

Heating the anilide (**1a**) in benzene or furan at 150 °C led to results fairly comparable to those obtained from the corresponding reactions at 85 °C, except that complete decomposition occurred within 15 h in both cases (Table 1). However, as can be seen in Table 1, in both cases there was a significant increase in the yield of the disulphide (**5a**) and a concomitant decrease in the overall yields of the products resulting from aromatic sulphenylation. These results would suggest that at 150 °C homolytic fission of the S-N bond would be an important competing reaction. Under these conditions the anilide (**1a**) was entirely decomposed in both neat cyclohexene and in furan in the presence of TEA to give the disulphide (**5a**) and 4-nitroaniline (**4a**) as the almost exclusive identifiable products (Table 1).

Decomposition of the parent benzenesulphenanilide (**1b**) and of 4'-methoxybenzenesulphenanilide (**1c**) was investigated in furan.

At 85 °C, decomposition of the anilide (**1b**) was found to be remarkably slower than that of the anilide (**1a**); after 30 days,



this reaction gave the disulphide (**5a**) (78%), 2'-(phenylthio)benzenesulphenanilide (**2b**) (4%), the (phenylthio)anilines (**3b**) and (**13a**) (3 and 5%), aniline (**4b**) (6%), and unchanged anilide (**1b**) (12%) in addition to much tarry material. At 150 °C, compound (**1b**) was completely decomposed within 15 h, to give disulphide (**5a**) (80%), aniline (**4b**) (28%) and the isomeric anilines (**3b**) and (**13a**) (3 and 4%) as the only identifiable products.

These results would indicate that decomposition of the anilide (**1b**) proceeds *via* homolytic fission of the S-N bond; however, the occurrence of the sulphenylated anilide (**2b**) might suggest some intervention of an ionic route, at least at 85 °C, despite our failure to observe any 2-(phenylthio)furan (**6**).

4'-Methoxybenzenesulphenanilide (**1c**) was found to remain largely unchanged at 85 °C for 30 days, only small amounts of the disulphide (**5a**), *p*-anisidine (**4c**), 2,7-dimethoxyphenazine (**14**), and 4,4'-dimethoxyazobenzene (**15**) being detected by t.l.c. These products were isolated in 80, 20, 5, and 8% yield respectively from the same reaction carried out at 150 °C, in which case complete decomposition of the anilide (**1c**) occurred within 15 h. The phenazine (**14**) and the azo compound (**15**) conceivably result from C<sub>ortho</sub>-N and N-N dimerisation of 4-methoxyanilanyl radicals.<sup>11</sup> Thus, the products of decomposition of anilide (**1c**) provided only indirect evidence of homolytic fragmentation.

The thermal reactivity trend exhibited by 4'-nitrophenyl-2-sulphenanilide (**1d**) was fully consistent with that observed with 4'-nitrobenzenesulphenanilide (**1a**). Upon heating in benzene at 85 °C, compound (**1d**) gave significant amounts of the sulphenylated anilide (**2d**) and the aniline (**3d**) in addition to traces of dibenzothiophene (**10**), the product expected from intramolecular electrophilic cyclisation of (**1d**);<sup>3b</sup> at 150 °C, comparable amounts of the aniline (**3d**) and (**10**) were formed in fair overall yield (Table 2).

These results would indicate that anilide (**1d**), analogously to (**1a**), can behave as an effective electrophilic species, to give intramolecular cyclisation and/or intermolecular reaction with another sulphenanilide unit. Moreover, thermolysis of compound (**1d**) at 150 °C in the presence of TEA led to the disulphide (**5b**) and 4-nitroaniline (**4a**) as the only identifiable products (Table 2). In the presence of TEA, the anilide (**1d**), analogously to (**1a**), can only undergo homolytic fragmentation.

The biphenyl-2-sulphenanilide (**1e**) in benzene at 85 °C exhibited chemical behaviour not dissimilar to that of the 4'-nitro-substituted analogue (**1d**) (Table 2). However, homolytic fission of the anilide bond appears to be the essential reaction at 150 °C; at this temperature, compound (**1e**) gave a poor yield of the isomeric anilines (**3e**) and (**13b**) [and no dibenzothiophene (**10**)]. Moreover, the product pattern and the reaction rate were not significantly affected by the addition of TEA (Table 2).

The thermal reactions of 4'-methoxybiphenyl-2-sulphenanilide (**1f**) in benzene at 85 and 150 °C led to results comparable to those of the anilide (**1c**) (Table 2).

The conclusions of the present study are that the 4'-substituted sulphenanilides (**1a**–**f**) exhibit two distinct reaction modes at 85 and 150 °C very dependent upon the nature of the 4'-substituent and the temperature employed: (i) nucleophilic displacement at the activated S–N bond of the corresponding conjugate acid possibly resulting from autoprotolysis, and (ii) homolysis of the S–N bond to give sulphenyl and anilino radicals. An increase in the electron-attracting capability of the 4'-substituent generally favours the ionic pathway, presumably as the result of an increase both in the acidity of the anilide proton, which would facilitate autoprotolysis of the anilide itself, and in the electrophilicity of the anilide bond. Homolytic S–N bond fragmentation is generally favoured by an increase in the reaction temperature.

## Experimental

Column chromatography was carried out on Merck silica gel (0.040–0.063 particle size) by elution with light petroleum (b.p. 40–70 °C) and diethyl ether–light petroleum mixtures (up to 100% diethyl ether). <sup>1</sup>H N.m.r. spectra were recorded at 60 MHz on a Varian T60 instrument for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as internal standard. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer and are for solutions in CS<sub>2</sub>. All m.p.s were measured on a Köfler apparatus and are uncorrected.

The sulphenanilides (**1a**–**c**)<sup>6a</sup> and (**1e**)<sup>3b</sup> were prepared by reaction of benzenesulphenyl or 2-phenylbenzenesulphenyl chloride, respectively, with the appropriate aniline. The hitherto unknown sulphenanilides (**1d**), (**1f**), and (**1g**) were similarly prepared in 40–70% yield.

All compounds (**1a**–**g**) were purified by column chromatography. 4'-Nitrobiphenyl-2-sulphenanilide (**1d**) had m.p. 158–159 °C;  $\nu_{\max}$ . 3 400 cm<sup>-1</sup>;  $m/z$  322 ( $M^+$ ), 185, and 184. 4'-Methoxybiphenyl-2-sulphenanilide (**1f**) had m.p. 101–102 °C;  $\nu_{\max}$ . 3 400 cm<sup>-1</sup>;  $m/z$  307 ( $M^+$ ), 186, 185, 184, and 122. *N*-Methyl-4'-nitrobenzenesulphenanilide (**1g**) had m.p. 79–80 °C;  $\nu_{\max}$ . 2 830, 1 340, 1 300, and 1 290 cm<sup>-1</sup>;  $m/z$  260 ( $M^+$ ), 218, 214, 152, 151, 110, and 109.

Reaction products such as the anilines (**4a**–**d**), the disulphides (**5a**) and (**5b**),<sup>3b</sup> dibenzothiophene (**10**), the arylthioanilines (**3b**),<sup>3a</sup> (**3e**),<sup>3b</sup> (**13a**),<sup>3a</sup> and (**13b**),<sup>3b</sup> 2-phenylthiofuran (**6**),<sup>12</sup> 2,7-dimethoxyphenazine (**14**),<sup>6a</sup> 4,4'-dimethoxyazobenzene (**15**),<sup>13</sup> and the arylamino sulphide (**7**)<sup>6b,c</sup> were each identified by spectral comparison with authentic specimens independently prepared or commercially available.

*Thermal Decomposition of Arenesulphenanilides (1a–g).*  
*General Procedure.*—A 0.2M solution of the arenesulphenanilide (**1a**–**g**) in the appropriate solvent (10 ml) without and with

added triethylamine (TEA) ( $3.3 \times 10^{-2}$  equiv.) was heated at 85 or 150 °C in a sealed tube. After a suitable reaction time, the excess of solvent was evaporated off and the residue was chromatographed on a silica gel column.

Reaction times and yields of identified products from the decomposition of the anilide (**1a**) in benzene, furan, cyclohexene, and 1M-cyclohexene in benzene and of the anilides (**1d**–**f**) in benzene are given in Tables 1 and 2, respectively. The following new compounds were obtained: 4'-nitro-2'-(phenylthio)benzenesulphenanilide (**2a**), m.p. 85–87 °C;  $\nu_{\max}$ . 3 340 (NH) and 1 330 cm<sup>-1</sup>;  $m/z$  354 ( $M^+$ ), 264, 245, 218, 200, 199, 198, and 109;  $\delta$  6.83–7.37 (10 H, m), 7.5 (1 H, d,  $J$  9 Hz), 8.27 (1 H, dd,  $J$  2.5 and 9 Hz), and 8.55 (1 H, d,  $J$  2.5 Hz) (Found: C, 61.35; H, 4.05; N, 7.8; S, 18.2. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires C, 61.0; H, 4.0; N, 7.9; S, 18.1%).

4-Nitro-2-(phenylthio)aniline (**3a**), m.p. 118–120 °C;  $\nu_{\max}$ . 3 520 and 3 400 (NH<sub>2</sub>) cm<sup>-1</sup>;  $m/z$  246 ( $M^+$ ), 216, 200, 199, 184, 183, 167, and 139;  $\delta$  5.1 (2 H, br s), 6.67 (1 H, d,  $J$  9 Hz), 7–7.4 (5 H, m), 8.1 (1 H, dd,  $J$  2.5 and 9 Hz), and 8.4 (1 H, d,  $J$  2.5 Hz) (Found: C, 58.35; H, 4.15; N, 11.3; S, 13.15. C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 58.5; H, 4.1; N, 11.4; S, 13.0%).

4-Nitro-2-phenylthio-N-[trans-2-(phenylthio)cyclohexyl]-aniline (**8**), m.p. 76–77 °C;  $\nu_{\max}$ . 3 360 (NH) and 1 340 cm<sup>-1</sup>;  $m/z$  436 ( $M^+$ ), 327, 285, 257, 238, 191, 181, 110, and 109;  $\delta$  (300 MHz) 1.1–2.2 (8 H, m), 2.95 (1 H, dt,  $J_d$  4 and  $J_t$  9.25 Hz), 3.38 (1 H, m, collapsing to dt,  $J_d$  4 and  $J_t$  9.25 Hz, upon D<sub>2</sub>O shake), 6.0 (1 H, d,  $J$  8.0 Hz, removed upon D<sub>2</sub>O shake), 6.48 (1 H, d,  $J$  9 Hz), 7.18–7.48 (10 H, m), 8.2 (1 H, dd,  $J$  2.5 and 9 Hz), and 8.54 (1 H, d,  $J$  2.5 Hz) (Found: C, 66.45; H, 5.6; N, 6.3; S, 14.55. C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires C, 66.0; H, 5.55; N, 6.4; S, 14.7%).

A compound which was probably *N*-(cyclohex-2-enyl)-4-nitroaniline (**9**), m.p. 98–99 °C;  $\nu_{\max}$ . 3 340 (NH) and 1 340 cm<sup>-1</sup>;  $m/z$  218 ( $M^+$ ), 190, and 81;  $\delta$  1.4–2.23 (6 H, m), 3.85–4.25 (1 H, m), 4.6 (1 H, br d, removed by D<sub>2</sub>O shake), 5.53–6.1 (2 H, m), 6.55 (2 H, d,  $J$  9 Hz), and 8.1 (2 H, d,  $J$  9 Hz).

2'-(Biphenyl-2-ylthio)-4'-nitrobiphenyl-2-sulphenanilide (**2d**), m.p. 68–70 °C;  $\nu_{\max}$ . 3 340 (NH) and 1 340 cm<sup>-1</sup>;  $m/z$  506 ( $M^+$ ), 370, 322, 185, 184, and 152 (Found: C, 71.35; H, 4.35; N, 5.65; S, 12.55. C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires C, 71.1; H, 4.4; N, 5.55; S, 12.65).

2-(Biphenyl-2-ylthio)-4-nitroaniline (**3d**), m.p. 164–165 °C;  $\nu_{\max}$ . 3 540 and 3 420 (NH<sub>2</sub>), and 1 350 cm<sup>-1</sup>;  $m/z$  322 ( $M^+$ ), 321, 275, 185, 184, and 152 (Found: C, 66.85; H, 4.45; N, 8.8; S, 9.85. C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 67.05; H, 4.4; N, 8.7; S, 9.95%).

2'-(Biphenyl-2-ylthio)-4'-methoxybiphenyl-2-sulphenanilide (**2f**), m.p. 95–98 °C;  $\nu_{\max}$ . 3 350 (NH) and 2 840 (OMe) cm<sup>-1</sup>;  $m/z$  491 ( $M^+$ ), 370, 307, 306, 185, 184, 152, 139, and 122 (Found: C, 75.6; H, 5.2; N, 2.85; S, 12.95. C<sub>31</sub>H<sub>23</sub>NOS<sub>2</sub> requires C, 75.75; H, 5.15; N, 2.85; S, 13.05%).

2-(Biphenyl-2-ylthio)-4-methoxyaniline (**3f**), m.p. 68–70 °C;  $\nu_{\max}$ . 3 480 and 3 380 (NH<sub>2</sub>) and 2 840 (OMe) cm<sup>-1</sup>;  $m/z$  307 ( $M^+$ ), 292, 279, 185, and 184 (Found: C, 74.4; H, 5.55; N, 4.5; S, 10.55. C<sub>19</sub>H<sub>17</sub>NOS requires C, 74.25; H, 5.6; N, 4.55; S, 10.45%).

4'-(Biphenyl-2-ylthio)biphenyl-2-sulphenanilide (**16**), m.p. 145–147 °C;  $\nu_{\max}$ . 3 400 (NH), 840, 750, and 710 cm<sup>-1</sup>;  $m/z$  461 ( $M^+$ ), 370, 368, 276, 275, 243, 185, 184, and 152 (Found: C, 78.25; H, 5.05; N, 3.0; S, 13.8. C<sub>30</sub>H<sub>23</sub>NS<sub>2</sub> requires C, 78.05; H, 5.0; N, 3.05; S, 13.9%). On treatment with 6M-hydrochloric acid<sup>6a</sup> compound (**16**) was essentially quantitatively converted into the aniline (**13b**) and the disulphide (**5b**), as indicated by t.l.c. (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>).

*Decomposition of 4'-Nitrobenzenesulphenanilide (1a) in Benzene at 85 °C in the Presence of TFA (0.2 Equiv.).*—This reaction was carried out for 24 h. After hydrolysis with 5% aqueous potassium carbonate and usual work-up, chromatography isolated (i) the disulphide (**5a**) (0.50 mmol, 56%); (ii) the sulphenylated anilide (**2a**) (0.054 mmol, 6%); (iii) phenyl benzenethiosulphonate<sup>6a</sup> (0.045 mmol, 5%); (iv) unchanged

(1a) (0.2 mmol, 10%); (v) the aniline (3a) (0.43 mmol, 24%); and (vi) 4-nitroaniline (4a) (0.83 mmol, 46%).

*Decomposition of 4'-Nitrobenzenesulphenanilide (1a) in Cyclohexene at 85 °C in the Presence of Boron Trifluoride-Diethyl Ether (0.1 Equiv).*—This reaction was carried out for 12 h, after which time t.l.c. (SiO<sub>2</sub>) showed absence of the starting material (1a) and formation of the arylamino sulphide (7) as the only detectable product.

*Decomposition of Benzenesulphenanilide (1b).*—(a) *In furan at 85 °C.* This reaction was carried out for 30 days, after which time chromatography gave (i) the disulphide (5a) (0.68 mmol, 78%); (ii) a compound which was probably 2'-(phenylthio)benzenesulphenanilide (2b) (0.035 mmol, 4%), m.p. 68–70 °C;  $\nu_{\max}$ . 3 360 (NH), 1 280, 755, 740, and 690 cm<sup>-1</sup>;  $m/z$  309 ( $M^+$ ), 218, 200, 199, 167, and 109. On treatment with 6M-hydrochloric acid compound (2b) was essentially quantitatively converted into the disulphide (5a) and the aniline (3b), as evidenced by t.l.c.

Continued elution gave (iii) unchanged anilide (1b) (0.24 mmol, 12%); (iv) 2-(phenylthio)aniline (3b) (0.053 mmol, 3%); (v) aniline (4b) (0.10 mmol, 6%); (vi) 4-(phenylthio)aniline (13a) (0.09 mmol, 5%); and (vii) an unidentified, dark brown product (40 mg).

(b) *In furan at 150 °C.* This reaction was carried out for 15 h. Chromatography afforded (i) the disulphide (5a) (0.8 mmol, 80%); (ii) 2-(phenylthio)aniline (3b) (0.06 mmol, 3%); (iii) aniline (4b) (0.56 mmol, 28%); (iv) 4-(phenylthio)aniline (13a) (0.08 mmol, 4%); and (v) tarry material.

*Decomposition of 4'-Methoxybenzenesulphenanilide (1c) in Furan at 150 °C.*—This reaction was carried out for 15 h. Chromatography gave (i) the disulphide (5a) (0.8 mmol, 80%); (ii) 4,4'-dimethoxyazobenzene (15) (0.08 mmol, 8%); (iii) 2,7-dimethoxyphenazine (14) (0.05 mmol, 5%); (iv) *p*-anisidine (4c) (0.4 mmol, 20%); and (v) tarry material.

*Decomposition of N-Methyl-4'-nitrobenzenesulphenanilide (1g).*—(a) *In benzene at 85 °C.* This reaction was carried out for 6 days, after which time chromatography gave (i) the disulphide (5a) (0.14 mmol, 14%); (ii) *N*-methyl-4-nitro-2-phenylthioaniline (3g) (1.66 mmol, 83%), m.p. 60–62 °C;  $\nu_{\max}$ . 3 400 (NH) and 1 330 cm<sup>-1</sup>;  $m/z$  260 ( $M^+$ ), 214, 199, and 91;  $\delta$  2.9 (3 H, d,  $J$  5 Hz, collapsing to br s upon D<sub>2</sub>O shake), 5.7 (1 H, br s, removed upon D<sub>2</sub>O shake), 6.57 (1 H, d,  $J$  9 Hz), 6.85–7.3 (5 H, m), 8.17 (1 H, dd,  $J$  2.5 and 9 Hz), and 8.37 (1 H, d,  $J$  2.5 Hz) (Found: C,

60.45; H, 4.6; N, 10.75; S, 12.2. C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 60.0; H, 4.65; N, 10.75; S, 12.3%); and (iii) *N*-methyl-4-nitroaniline (4d) (0.3 mmol, 15%).

(b) *In furan at 85 °C.* This reaction was carried out for 6 days. Chromatography gave (i) the disulphide (5a) (0.06 mmol, 25%); (ii) 2-(phenylthio)furan (6) (0.192 mmol, 40%); (iii) unchanged anilide (1g) (1.52 mmol, 76%); (iv) compound (3g) (0.019 mmol, 4%); and (v) the aniline (4d) (0.38 mmol, 79%).

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### References

- 1 T. Zincke and K. Eismayer, *Chem. Ber.*, 1918, **51**, 751.
- 2 M. L. Moore and T. B. Johnson, *J. Am. Chem. Soc.*, 1935, **57**, 1517, 2234; 1936, **58**, 1091, 1960.
- 3 (a) F. A. Davis, E. R. Fretz, and C. J. Horner, *J. Org. Chem.*, 1973, **38**, 690; (b) F. A. Davis, C. J. Horner, E. R. Fretz, and J. F. Stackhouse, *ibid.*, 695; (c) F. A. Davis, R. B. Wetzels, T. J. Devon, and J. F. Stackhouse, *ibid.*, 1971, **36**, 799; (d) F. A. Davis and R. P. Johnston II, *ibid.*, 1972, **37**, 854.
- 4 T. Ando, M. Nojima, and N. Tokura, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2227.
- 5 P. Ainpour and N. E. Heimer, *J. Org. Chem.*, 1978, **43**, 2061.
- 6 (a) L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2261; (b) *Tetrahedron Lett.*, 1984, **25**, 2039; (c) *Tetrahedron*, 1986, **42**, 1145.
- 7 (a) L. Benati, C. M. Camaggi, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1972, 2817; (b) L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *Gazz. Chim. Ital.*, 1975, **105**, 841; (c) L. Benati, C. M. Camaggi, and G. Zanardi, *J. Org. Chem.*, 1975, **40**, 966.
- 8 D. H. R. Barton, T. Nakano, and P. G. Sammes, *J. Chem. Soc. C*, 1968, 322.
- 9 L. Benati, P. C. Montevecchi, and P. Spagnolo, unpublished data.
- 10 P. Brownbridge, *Tetrahedron Lett.*, 1984, **25**, 3759; A. Bewick, D. E. Coe, J. M. Mellor, and W. M. Owton, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1033.
- 11 L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1982, 3049 and references therein.
- 12 D. G. Manly and E. D. Amstutz, *J. Org. Chem.*, 1956, **21**, 516.
- 13 L. Horner and J. Dehnert, *Chem. Ber.*, 1963, **96**, 786.

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