Acid-promoted Decomposition of Benzenesulphenanilides and *N*-Aryl Bis(benzenesulphen)amides

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The decomposition of 4'-substituted benzenesulphenanilides (**1a—d**) in the presence of trifluoroacetic acid (0.6 equiv.) leads to *N*-arylbis(benzenesulphen)amides (**6a—d**) in variable yields, depending on the 4'-substituent, in addition to disulphide (**4**) and anilines (**3a—d**), whereas products arising from sulphenylation of the *N*-aryl ring result from 3'-methoxybenzenesulphenanilide (**1g**). The 4'-nitro- and 3'-nitro-benzenesulphenanilides (**1e,f**) react with a slight excess of trifluoroacetic acid to give only (**4**), the thiosulphonate (**5**), and aniline (**3e,f**). The findings are interpreted in terms of possible nucleophilic attack at the S–N bond of a protonated sulphenanilide by the nitrogen or the *N*-aryl ring of another sulphenanilide unit, according to the nature of the substituent and its position, with displacement of aniline (**3**). The reaction of (**1a—d**) with 1.5 equiv. of trifluoroacetic acid leads to complete disappearance of the initially formed amides (**6a—d**) with concomitant formation of phenazines (**9**) and/or *p*-quinone di-imines (**8**). Similar results are obtained by using boron trifluoride–diethyl ether. Di-imines (**8**) and phenazines (**9**) are explained on the basis of a mechanism initially involving nucleophilic attack by (**1**) and/or (**6**) and/or (**3**) at the *ortho* and *para* positions of an intermediate cation, possibly (**18A**) or (**18B**), and loss of the disulphide (**4**).

Sulphenamides are compounds of considerable interest both from a practical as well as a theoretical point of view, because of the peculiar nature of the S–N bond, which permits a variety of important reactions with both electrophilic and nucleophilic species.[1] In particular, the reactions of sulphenamides with electrophiles generally result in S–N cleavage through co-ordination of the electrophile with the nitrogen lone pair followed by nucleophilic attack on the activated S–N bond.[1,2]

Most recently we have reported[3] the preliminary results of a study of the boron trifluoride–diethyl ether promoted decomposition of a series of substituted benzenesulphenanilides (**1a—g**) in the presence of alkenes, which showed that compounds (**1**) are rapidly destroyed under these conditions, generally leading to β-arylamino sulphides in yields dependent on both the nature of the *N*-aryl substituent and the alkene employed; moreover, we have observed that trifluoroacetic acid (TFA) can induce a rapid decomposition of the anilides (**1**) in the presence of alkenes, generally resulting in the formation of β-trifluoroacetoxy sulphides.[4] In the course of this investigation we noticed that compounds (**1**) suffer acid-promoted decomposition in the absence of alkenes in a fashion largely influenced by the *N*-aryl substituent with respect to both the rates of decomposition and the nature of the resulting products. These findings prompted us to undertake a study of the reaction of (**1a—g**) with TFA and boron trifluoride–diethyl ether since it was of interest to us to explore the effects of the substituent and the acid with the view of throwing light on the possible mechanism of these reactions.

RNHSPh (1) $R\overset{+}{N}H_2SPh$ (2) RNH_2 (3)

PhSSPh (4) $PhSO_2Ph$ (5) $RN(SPh)_2$ (6)

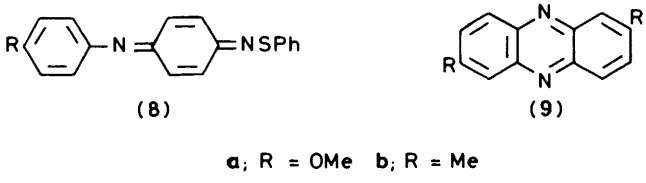
$R\overset{+}{N}H(SPh)_2$ (7)

a; R = C_6H_4OMe-*p* f; R = $C_6H_4NO_2$-*m*
b; R = C_6H_4Me-*p* g; R = C_6H_4OMe-*m*
c; R = Ph h; R = $C_6H_4CH_2CH_2Ph$-*m*
d; R = C_6H_4Cl-*p* i; R = C_6H_4Ph-*o*
e; R = $C_6H_4NO_2$-*p*

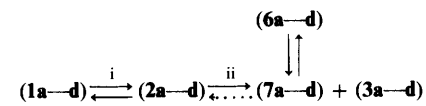
Results and Discussion

Treatment of a benzene solution of the benzenesulphenanilides (**1a—d**) (0.05M) with 0.6 equiv. of TFA at room temperature for *ca.* 7—30 min led, after hydrolysis of the resulting reaction mixtures and column chromatography, to the isolation of the anilines (**3a—d**) (20—63%), the diphenyl disulphide (**4**) (32—50%), and the *N*-arylbis(benzenesulphen)amides (**6a—d**) (32—54%) as well as unchanged starting material (18—44%) and small amounts of the *p*-quinone di-imines (**8**) and/or the 2,7-disubstituted phenazines (**9**) (Table 1).

The mechanism for the formation of the amides (**6a—d**) most likely involves nucleophilic attack by the nitrogen of (**1a—d**) at the activated S–N bond of a protonated sulphenanilide unit (**2a—d**) to give elimination of aniline (**3a—d**) (Scheme 1).



a; R = OMe b; R = Me
c; R = H d; R = Cl



Scheme 1. *Reagents:* i, TFA, benzene; ii, +(**1a—d**)

A similar mechanism has been previously suggested by Davis *et al.*[1b] for the decomposition of a number of sulphenamides promoted by acetic acid or boron trifluoride.

Table 1. Yields (%)[a] of products from the decomposition of benzenesulphenanilides (**1a**—**d**) in the presence of TFA (0.6 equiv.)[b]

Sulphenanilide	Reaction time (min)	Conversion (%)	Aniline[c]	Diphenyl disulphide (**4**)	Bis(sulphen)-amide	Quinone di-imine	Phenazine
(**1a**)	7	82	34 (**3a**)	32	54 (**6a**)	4 (**8a**)	2 (**9a**)
(**1b**)	7	72	46 (**3b**)	50	46 (**6b**)		5 (**9b**)
(**1c**)	7	63	20 (**3c**)	44	35 (**6c**)	2 (**8c**)	
(**1d**)	30	56	63 (**3d**)	42	32 (**6d**)		3 (**9d**)

[a] Yields based on 2 mol of reacted (**1**) giving 1 mol each of the products, unless otherwise stated. [b] Reactions were carried out at 25 °C in benzene. [c] Yields based on 1 mol of reacted (**1**) giving 1 mol of the product (**3**).

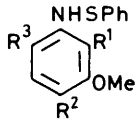
Table 2. Yields (%)[a,b] of products from the decomposition of benzenesulphenanilides (**1a**—**f**) in the presence of TFA (1.5 equiv.) or BF_3·Et_2O (1.5 equiv.)[c]

Sulphenanilide	Aniline[d]	Diphenyl disulphide (**4**)	Benzenethio-sulphonate (**5**)	Quinone di-imine	Phenazine
(**1a**)	22 (**3a**)	80		32 (**8a**)	10 (**9a**)
(**1b**)	55 [52] (**3b**)	94 [90]			35 [28] (**9b**)
(**1c**)	25 [23] (**3c**)	78 [82]		24 [26] (**8c**)	4 [n.d.] (**9c**)
(**1d**)	55 [63] (**3d**)	88 [82]		1 [1] (**8d**)	34 [30] (**9d**)
(**1e**)	98 [90] (**3e**)	56 [78]	32 [n.d.]		
(**1f**)	86 [68] (**3f**)	70 [64]	16 [n.d.]		

[a] Yields based on 2 mol of (**1**) giving 1 mol of each of the products, unless otherwise stated. [b] Figures in square brackets refer to reactions carried out in the presence of BF_3·Et_2O. [c] Reactions were run at 25 °C in benzene. [d] Yields based on 1 mol of (**1**) giving 1 mol of the product (**3**).

As can be seen from Table 1, both the extent of the conversion of the anilides (**1a**—**d**) and the yields of the resulting amides (**6a**—**d**) decrease progressively on passing from (**1a**) to (**1d**) as a consequence of the progressive decrease in the electron-donating effect of the 4′-substituent.

The reaction of 3′-methoxybenzenesulphenanilide (**1g**) with 0.6 equiv. of TFA resulted in 70% decomposition of (**1g**) within *ca.* 7 min leading to the formation of 2′-phenylthio-5′-methoxybenzenesulphenanilide (**10c**) (42%) in addition to two products, (**I**) and (**II**) (4 and 9%). The latter were probably the anilides (**10a**) and (**10b**), though definite structural assignments

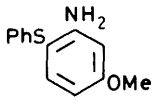


(10a) R^1 = SPh, R^2 = R^3 = H

(10b) R^1 = R^3 = H, R^2 = SPh

(10c) R^1 = R^2 = H, R^3 = SPh

(11) R^1 = H, R^2 = R^3 = SPh



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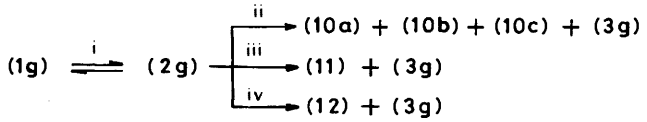


Scheme 2. *Reagents:* i, TFA, benzene; ii, +(**1g**), $-H^+$; iii, +(**10b**) and/or (**10c**), $-H^+$; iv, + (**3g**), $-H^+$

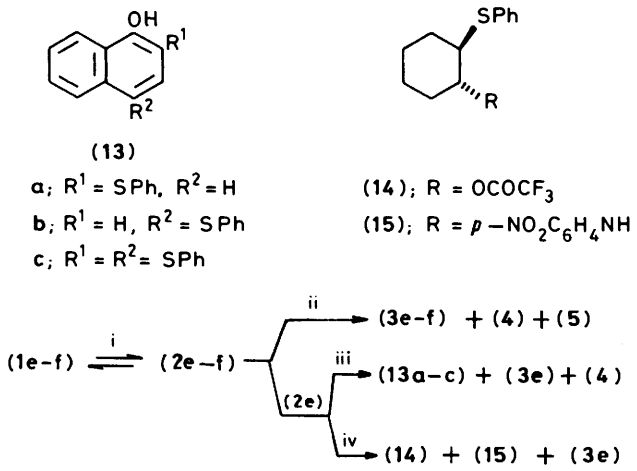
were not made; *m*-anisidine (**3g**) (22%) together with minor amounts of the disulphide (**4**) (8%), 2′,4′-bisphenylthio-5′-methoxybenzenesulphenanilide (**11**) (7%), and the aniline (**12**) (2%) were also produced.

The structural assignment of (**10c**) was made on the basis of chemical evidence in addition to elemental analysis and spectral data; in fact, on treatment with 6M-hydrochloric acid the sulphenanilide (**10c**) was readily converted into the known aniline (**12**). As for products (**I**) and (**II**), their spectral data appeared to be consistent with both structures (**10a**) and (**10b**); on the other hand, treatment of (**I**) and (**II**) with 6M-hydrochloric acid and subsequent treatment with pentyl nitrite led ultimately to 2-methoxyphenyl phenyl sulphide in both cases. The benzenesulphenanilides (**10a**—**c**) can be reasonably assumed to have arisen from sulphenylation of the *N*-aryl ring of (**1g**) by (**2g**), compound (**11**) being the product of further sulphenylation of (**10b**) and/or (**10c**) (Scheme 2). Thus the presence of the strongly electron-donating methoxy substituent *meta* to the NHSPh group causes a preferential activation of the *N*-phenyl ring of (**1g**) with respect to the sulphenanilide nitrogen towards attack at the S–N bond of (**2g**).

Although the 4′-nitro- and 3′-nitro-benzenesulphenanilides (**1e**) and (**1f**) were stable for several hours in the presence of 0.6 equiv. of TFA, in the presence of a slight excess (1.5 equiv.) they were completely decomposed within *ca.* 24 h to give the disulphide (**4**) (56—70%), phenyl benzenethiosulphonate (**5**) (16—32%), and the corresponding aniline (**3e**—**f**) (86—98%) (Table 2). This shows that the sulphenanilides (**1e**) and (**1f**) are too weakly nucleophilic to enable nucleophilic displacement to take place at the sulphur of (**2e**—**f**), so that attack by the poorly nucleophilic trifluoroacetate ion to afford (**3e**—**f**) and $PhSOCOCF_3$, and, subsequently by hydrolysis, the disulphide (**4**) and the benzenethiosulphonate (**5**) would occur.[5]

This view is supported by the results obtained from the reaction of (**1e**) with 1.5 equiv. of TFA carried out both in benzene in the presence of equivalent amounts of 1-naphthol and in cyclohexene; in each case complete disappearance of (**1e**) occurred within 10 min.

In the presence of 1-naphthol, (**1e**) gave the sulphenylation products (**13a**), (**13b**), and (**13c**) (42, 33, and 10%, respectively), whereas in cyclohexene the *trans* adducts (**14**) and (**15**) were formed in 71 and 24% yields, respectively[3,4] (Scheme 3).



Scheme 3. *Reagents:* i, TFA; ii, benzene; iii, 1-naphthol, benzene; iv, cyclohexene

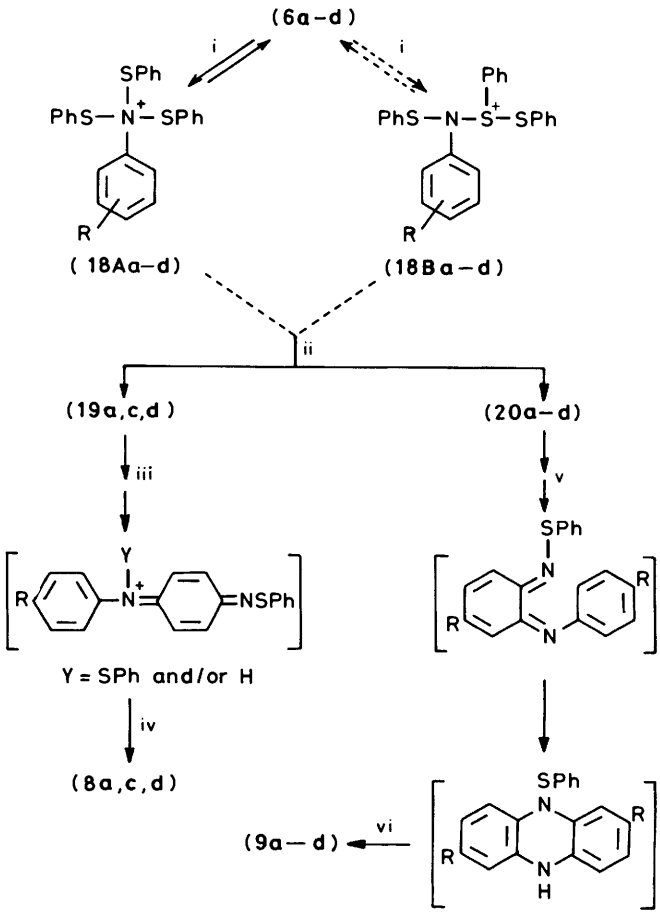
The occurrence of the di-imines (**8**) and/or the phenazines (**9**) in the reaction of the anilides (**1a—d**) with 0.6 equiv. of TFA is ascribable to some decomposition of the imides (**6a—d**) as supported by our findings that in the presence of an excess of TFA (1.5 equiv.) the anilides (**1a—d**) suffered complete decomposition in a few minutes to give the *p*-quinone di-imines (**8a—d**) (0—32%) and the 2,7-disubstituted phenazines (**9a—d**) (4—35%) in addition to the anilines (**3a—d**) and the disulphide (**4**); the amides (**6a—d**) could not be isolated, but were clearly shown by t.l.c. to be initially formed (Table 2). Further support comes from the reactions of the amides (**6a**) and (**6c**) with 1.5 equiv. of TFA, which gave (**8a**) and (**9a**) (46 and 7%) and (**8c**) and (**9c**) (20 and 3%), respectively.

In view of the fact that both phenazines (**9**) and di-imines (**8**) have been recently shown to be produced through a free-radical mechanism involving benzenesulphenanilidyl radicals (**16**),[6] we investigated the possible involvement of such radicals [or the corresponding radical cations (**17**)] in the TFA-promoted

decomposition of (**6**). The reaction of the amide (**6a**) with TFA (1.5 equiv.) in benzene was carried out in the cavity of an e.s.r. spectrometer; no radical signals could be detected. On this basis, we suggest that the formation of the phenazines (**9**) and the di-imines (**8**) might be explained in terms of an ionic route initially involving nucleophilic attack at some electrophilic intermediate, possibly the anilinium ion (**18A**) or the azasulphonium ion (**18B**), produced from the amides (**6**) under the reaction conditions, by any nitrogen nucleophile present in the reaction medium [*i.e.* (**1**), (**3**), and (**6**)].

In fact, nucleophilic attack at the *para* position of the *N*-aryl ring of the possible intermediates (**18a, c, d**) and loss of disulphide (**4**) might lead to (**19a, c. d**) and then ultimately to the corresponding di-imines (**8a, c, d**), presumably according to the sequence outlined in Scheme 4.

On the other hand, nucleophilic attack at the corresponding *ortho* position of (**18a—d**) [and loss of (**4**)] might afford (**20a—d**), which would presumably be precursors of the 2,7-disubstituted phenazines (**9a—d**), possibly resulting from the sequence of reactions outlined in Scheme 4.[6,7] The postulated



Scheme 4. *Reagents:* i, +(**2a—d**), −(**3a—d**) and/or +(**7a—d**), −(**1a—d**); ii, +(**1a—d**) and/or +(**3a—d**) and/or +(**6a—d**), −(**4**); iii, −PhSR and/or −HR; iv, −PhS^+ and/or $-H^+$; v, −PhS^+, −PhSH and/or $-H^+$, −PhSH and/or $-H^+$, −2H; vi, −PhSH

intermediacy of the anilinium ion (**18A**) in the formation of (**8**) and (**9**) is essentially based on the assumption that the amides (**6**) display chemical behaviour analogous to that of the anilides (**1**) and thus can both be sulphenylated at the nitrogen and act as effective sulphenylating agents in their protonated forms (**7**).

However, intermediacy of the azasulphonium ion (**18B**) in the formation of (**8**) and (**9**) is, in our opinion, also conceivable; in fact, some competing sulphenylation of (**6**) at one sulphur might reasonably occur to give (**18B**), which might then be the species actually involved in the formation of (**8**) and (**9**).

Morever, we wish to point out that the postulated intermediate ions (**18A**) or (**18B**) can both be regarded as potential precursors of *N*-sulphenylarylnitrenium ions which

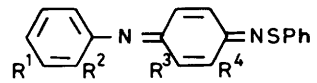
might, in principle, result from (**18A**) or (**18B**) by unimolecular loss of disulphide (**4**). To our knowledge, sulphenylnitrenium ions have not as yet been reported, though arylnitrenium ions (and their precursors) have reportedly been produced in a variety of reactions and have been shown to be trapped at the nitrogen and/or at the ring positions by a number of nucleophiles.[8] The evidence provided by the reactions of the amides (**6a**) and (**6b**) with TFA (3 equiv.), carried out in the presence of 2 mol. equiv. of the anilines (**3b**) and (**3a**), respectively, was consistent with our suggested mechanism. In the presence of *p*-toluidine (**3b**) the *N*-(*p*-methoxyphenyl)-bis(benzenesulphen)amide (**6a**) furnished a mixture of *N*-(*p*-methoxyphenyl)-*N'*-phenylthio- and *N*-(*p*-tolyl)-*N'*-phenylthio-*p*-benzoquinone-di-imines (**8a**) and (**8b**) (13 and 28%) together with the anilide (**1b**), the disulphide (**4**), *p*-anisidine (**3a**), and small amounts of 2,7-dimethoxyphenazine (**9a**).

The occurrence of the di-imine (**8b**) accompanying the di-imine (**8a**) can be explained by assuming that the possible intermediate ion (**18a**) undergoes attack by *p*-toluidine (**3b**) [and/or the corresponding anilide (**1b**) produced under the reaction conditions by sulphenylation of (**3b**)] to give ultimately (**8b**); this would occur in competition with attack by (**3a**) [and/or (**1a**) and/or (**6a**)], which would afford the di-imine (**8a**). On the other hand, the reaction of *N*-(*p*-tolyl)-bis(benzenesulphen)amide (**6b**) in the presence of *p*-anisidine (**3a**) gave a mixture of 2-methoxy-7-methylphenazine (15%) and 2,7-dimethylphenazine (**9b**) (25%) together with the anilides (**1a, b**), *p*-toluidine (**3b**), and disulphide (**4**).

In this case, the concomitant formation of the phenazine (**9b**) and the crossed 2-methoxy-7-methylphenazine might be explained in terms of competing reactions of the intermediate (**18b**) with (**3b**) [and/or (**1b**) and/or (**6b**)] and (**3a**) [and/or (**1a**)].

Our attempts to find further support for the mechanism suggested for the TFA-promoted decomposition of (**6**) by exploring the reaction of the amides (**6a**) and (**6c**) with TFA in the presence of 1-naphthol in the hope of finding evidence of the interception of such a nucleophile by the postulated intermediates (**18a**) and (**18c**), were unsuccessful. In fact, qualitative experiments showed that the amides (**6a**) and (**6c**) react with TFA (1.5 equiv.) in the presence of equimolar amounts of 1-naphthol to give the sulphenylation products (**13a—c**), in addition to the corresponding anilines (**3a, c**) and minor amounts of disulphide (**4**); concomitant suppression of the di-imines (**8a**) and (**8c**) as well as of the phenazines (**9a**) and (**9c**) was observed. Effective trapping of the protonated amides (**7a**) and (**7c**) by the naphthol ring [and of the protonated anilides (**2a**) and (**2c**) thus resulting] would essentially occur under these circumstances.

Furthermore, we also prepared the benzenesulphenanilides (**1h**) and (**1i**) and studied their decomposition in the presence of 1.5 equiv. of TFA in order to ascertain whether the possible intermediates (**18h**) and (**18i**) might have been induced to



(**8h**) $R^1 = R^3 = CH_2CH_2Ph, R^2 = R^4 = H$

(**8i**) $R^1 = R^3 = H, R^2 = R^4 = Ph$

undergo intramolecular nucleophilic trapping at the *ortho* and *para* positions by the phenyl ring of the *meta* phenylethyl substituent and/or at the nitrogen by the adjacent phenyl ring, respectively.

However, the decomposition of the anilides (**1h**) and (**1i**) led to rather complex reaction mixtures, from which the disulphide (**4**) (75—78%), the anilines (**3h, i**) (42—52%), and probably the compounds (**8h**) and (**8i**) (20 and 18%), the di-imine analogues of (**8a—d**), could be isolated as the only identifiable products.

Finally, in order to ascertain the possible effect of using a Lewis acid such as boron trifluoride in place of TFA, we have also investigated the reaction of the anilides (**1b—f**) with 1.5 equiv. of boron trifluoride–diethyl ether in benzene. These reactions led to results generally comparable with those obtained from the corresponding reactions with TFA, except that the decomposition of the anilides (**1e**) and (**1f**) was found to be remarkably accelerated [anilides (**1e**) and (**1f**) were entirely destroyed in *ca.* 3 h] and no formation of the benzenethiosulphonate (**5**) was observed in these cases (Table 2). On this basis, we suggest that the BF_3-promoted decomposition of (**1**) [and (**6**)] be described in terms of a mechanism essentially similar to that postulated for the corresponding reactions with TFA, provided that co-ordination of the nitrogen atom of (**1**) [and (**6**)] with boron trifluoride be assumed instead of protonation.

Experimental

The benzenesulphenanilides (**1a—f**)[6a-b,9] were prepared by allowing benzenesulphenyl chloride to react with the corresponding anilines. The benzenesulphenanilides (**1g**), (**1h**), and (**1i**) were similarly prepared in 50—60% yields from benzenesulphenyl chloride and *m*-anisidine (**3g**), 3-aminobibenzyl (**3h**),[10] and 2-aminobiphenyl (**3i**), respectively.

3'-Methoxybenzenesulphenanilide (**1g**) was a thick oil; $\nu_{max.}$ 3 440 cm^{-1}; *m/z* 231 (M^+), 198, 122, 109, and 95; δ 3.63 (3 H, s), 5.15 (1 H, s), and 6.4—7.3 (9 H, m). 3-Phenethylbenzenesulphenanilide (**1h**) was a thick oil; $\nu_{max.}$ 3 420 cm^{-1}; *m/z* 305 (M^+), 214, 197, 196, and 181; δ 2.9 (4 H, s), 5.1 (1 H, s), and 6.8—7.3 (14 H, m). 2'-Phenylbenzenesulphenanilide (**1i**) had m.p. 72—73 °C; $\nu_{max.}$ 3 410 cm^{-1}; *m/z* 277 (M^+), 168, and 167. Reaction products, such as the anilines (**3a—i**), 2-phenylthio-5-methoxyaniline (**12**),[11] diphenyl disulphide (**4**), phenyl benzenethiosulphonate (**5**),[12] the bis(benzenesulphen)amides (**6a**),[6a] (**6c**),[6b] and (**6d**),[6b] the *p*-benzoquinone di-imines (**8a**),[6c] (**8c**),[6b] and (**8d**),[6b] the phenazines (**9a**),[6a] (**9b**),[13] (**9c**), and (**9d**)[6b] were each identified by spectral comparison with authentic specimens independently prepared or commercially available. 2-Methoxy-7-methylphenazine,[14] 2-phenylthio-1-naphthol (**13a**),[15] and 4-phenylthio-1-naphthol (**13b**)[16] were characterized on the basis of physical and spectral properties.

Yields of reaction products from the decomposition of the benzenesulphenanilides (**1a—d**) with 0.6 equiv. of TFA and from the decomposition of the benzenesulphenanilides (**1a—f**) with 1.5 equiv. of TFA or $BF_3 \cdot Et_2O$ are given in Tables 1 and 2, respectively.

Column chromatography was carried out on Merck silica gel (0.040—0.063 particle size) by gradual elution with light petroleum (b.p. 40—70 °C)–diethyl ether (20:80). ^1H N.m.r. spectra are for solutions in $CDCl_3$, i.r. spectra are for solutions in CCl_4. G.l.c. analyses were performed on a Varian 3700 instrument using a 5% SP 2250 Supelcoport column.

Acid-promoted Decomposition of Benzenesulphenanilides (**1a—i**) *and Bis(benzenesulphen)amides* (**6a—c**): *General Procedure.*—To a solution of the appropriate benzenesulphenanilide (**1**) or bis(benzenesulphen)amide (**6**) (4 mmol) in benzene (80 ml) trifluoroacetic acid (2.4 mmol, 0.2 ml, or 6 mmol, 0.5 ml) or boron trifluoride–diethyl ether *ca.* 47% BF_3 (6 mmol, 0.75 ml) was added under vigorous stirring at room temperature; in all cases, except for the anilides (**1e, f**), the resulting reaction mixtures became immediately dark blue. After being stirred for the appropriate time (from 7 min up to 24 h, according to the reaction conditions and the starting benzenesulphenanilide or

amide), the reaction mixture was treated with 5% aqueous potassium carbonate; the organic layer was then separated, the excess solvent removed under reduced pressure and the residue chromatographed unless otherwise stated. The TFA promoted decompositions of the anilide (**1e**) in the presence of 1-naphthol and the amides (**6a**) and (**6b**) in the presence of *p*-toluidine (**3b**) and *p*-anisidine (**3a**) were similarly carried out by adding the appropriate amount of TFA to the appropriate benzene solution of (**1e**) and 1-naphthol, (**6a**) and *p*-toluidine (**3b**), and (**6b**) and *p*-anisidine (**3a**), respectively.

Decomposition of 4'-Methoxybenzenesulphenanilide (**1a**).—(a) *With* 0.6 *equiv. of TFA*. Hydrolysis (after 7 min) and then chromatography isolated (i) diphenyl disulphide (**4**); (ii) the amide (**6a**); (iii) starting material (**1a**) (18%); (iv), *N*-(*p*-methoxyphenyl)-*N'*-phenylthio-*p*-benzoquinone di-imine (**8a**); (v) *p*-anisidine (**3a**); and (vi) 2.7-dimethoxyphenazine (**9a**).

(b) *With* 1.5 *equiv. of TFA*. Hydrolysis (after 10 min) and then chromatography gave (i) the disulphide (**4**); (ii) the di-imine (**8a**); (iii) *p*-anisidine (**3a**); (iv) phenazine (**9a**); and (v) a mixture of unidentifiable, coloured products.

Decomposition of 4'-Methylbenzenesulphenanilide (**1b**).—(a) *With* 0.6 *equiv. of TFA*. Hydrolysis (after 7 min) and then chromatography gave (i) the disulphide (**4**); (ii) N-(p-*tolyl*)-*bis*(*benzenesulphen*)*amide* (**6b**), m.p. 106—107 °C; $\nu_{max.}$ 1 490, 1 450, 1 215, 1 185, 900, and 695 cm^{-1}; δ 2.2 (3 H, s) and 6.9—7.5 (14 H, m); *m/z* 218, 215, 214, 109, 106 (Found: C, 71.05; H, 5.25; N, 4.4; S, 19.6. $C_{19}H_{17}NS_2$ requires C, 70.55; H, 5.3; N, 4.35; S, 19.8%); (iii) the starting material (**1b**) (28%); (iv) 2,7-dimethylphenazine (**9b**); and (v) *p*-toluidine (**3b**).

(b) *With* 1.5 *equiv. of TFA*. Hydrolysis (after 10 min) and then chromatography gave (i) the disulphide (**4**); (ii) the phenazine (**9b**); and (iii) *p*-toluidine (**3b**).

(c) *With* 1.5 *equiv. of* BF_3. Hydrolysis (after 7 min) and then column chromatography afforded (i) the disulphide (**4**); (ii) the phenazine (**9b**); (iii) *p*-toluidine (**3b**); and (iv) tarry material.

Decomposition of Benezenesulphenanilide (**1c**).—(a) *With* 0.6 *equiv. of TFA*. Hydrolysis (after 7 min) and then chromatography gave (i) the disulphide (**4**); (ii) *N*-phenylbis(benzenesulphen)amide (**6c**); (iii) starting material (**1c**) (37%); (iv) the di-imine (**8c**); and (v) aniline (**3c**).

(b) *With* 1.5 *equiv. of TFA*. Hydrolysis (after 10 min) and then chromatography gave (i) the disulphide (**4**); (ii) the di-imine (**8c**); (iii) the phenazine (**9c**); (iv) aniline (**3c**); and (v) unidentifiable, tarry products.

(c) *With* 1.5 *equiv. of* BF_3. Hydrolysis (after 7 min) and then chromatography gave (i) the disulphide (**4**); (ii) the di-imine (**8c**); (iii) phenazine (**9c**); (iv) aniline (**3c**); and (v) tarry material.

Decomposition of 4'-Chlorobenzenesulphenanilide (**1d**).—(a) *With* 0.6 *equiv. of TFA*. Hydrolysis (after 35 min) and then chromatography isolated (i) the disulphide (**4**); (ii) *N*-(4-chlorophenyl)bis(benzenesulphen)amide (**6d**); (iii) unchanged (**1d**) (44%); (iv) 2,7-dichlorophenazine (**9d**); and (v) *p*-chloroaniline (**3d**).

(b) *With* 1.5 *equiv. of TFA*. Hydrolysis (after 10 min) and then chromatography gave (i) the disulphide (**4**); (ii) the phenazine (**9d**); (iii) the di-imine (**8d**); and (iv) aniline (**3d**). Continued elution furnished intractable material.

(c) *With* 1.5 *equiv. of* BF_3. Hydrolysis (after 7 min) and then chromatography furnished (i) the disulphide (**4**); (ii) the phenazine (**9d**); (iii) the di-imine (**8d**); and (iv) the aniline (**3d**). Continued elution gave tarry material.

Decomposition of 4'-Nitrobenzenesulphenanilide (**1e**).—(a) *With* 1.5 *equiv. of TFA*. Complete disappearance of starting (**1e**) occurred after *ca.* 24 h (t.l.c.). After work-up of the reaction mixture, chromatography gave (i) the disulphide (**4**); (ii) phenyl benzenethiosulphonate (**5**); and (iii) *p*-nitroaniline (**3e**).

(b) *With* 1.5 *equiv. of* BF_3. Complete absence of starting material was noticed after *ca.* 3 h (t.l.c.). After work-up, quantitative g.l.c. analysis of the reaction mixture gave the disulphide (**4**) and *p*-nitroaniline (**3e**).

(c) *With* 1.5 *equiv. of TFA in the presence of* 1-*naphthol* (1 *equiv.*). Hydrolysis (after 10 min) and then chromatography gave (i) the disulphide (**4**) (0.29 mmol, 14%); (ii) 2-phenylthio-1-naphthol (**13a**) (1.68 mmol, 42%), as thick oil; $\nu_{max.}$ 3 440br cm^{-1} (OH); *m/z* 252 (M^+), 219, 174, and 146; δ 7.1 (5 H, s), 7.17 (1 H, s, removed by D_2O shake), 7.3—7.87 (5 H, m), and 8.15—8.5 (1 H, m); (iii) 2,4-*bis*(*phenylthio*)-1-*naphthol* (**13c**) (0.20 mmol, 10%), as thick oil; $\nu_{max.}$ 3 430br cm^{-1} (OH); *m/z* 360 (M^+), 283, 282, 251, 221; δ 6.9—7.23 (10 H, m), 7.28 (1 H, s, removed by D_2O shake), 7.28—7.65 (2 H, m), 7.85 (1 H, s), and 8.15—8.5 (2 H, m) (Found: C, 72.5; H, 4.35; S, 18.95. $C_{22}H_{16}OS_2$ requires C, 73.3; H, 4.45; S, 18.8%); (iv) 4-phenylthio-1-naphthol (**13b**) (1.31 mmol, 33%), as thick oil; $\nu_{max.}$ 3 620sh (strong) and 3 350br (weak) cm^{-1} (OH); *m/z* 252 (M^+), 219, and 144; δ 4.1 (1 H, s, removed by D_2O shake); 6.75 (1 H, d, *J* 8 Hz), 7.05—7.85 (8 H, m), and 8.15—8.6 (2 H, m); and (v) *p*-nitroaniline (**3e**) (3.9 mmol, 98%).

Decomposition of 3'-Nitrobenzenesulphenanilide (**1f**).—(a) *With* 1.5 *equiv. of TFA*. Disappearance of the starting material (**1f**) was found to be complete after *ca.* 24 h (t.l.c.). After work-up of the reaction mixture, chromatography gave (i) the disulphide (**4**); (ii) benzenethiosulphonate (**5**); and (iii) *m*-nitroaniline (**3f**).

(b) *With* 1.5 *equiv. of* BF_3. Complete disappearance of starting material (**1f**) was noticed after *ca.* 3 h (t.l.c.). After work-up of the reaction mixture, quantitative g.l.c. analysis gave the disulphide (**4**) and *m*-nitroaniline (**3f**).

Decomposition of 3'-Methoxybenzenesulphenanilide (**1g**) *with* 0.6 *Equiv. of TFA*.—Hydrolysis (after 7 min) and then chromatography afforded (i) the disulphide (**4**) (0.11 mmol, 8%); and (ii) 2'-*phenylthio*-5'-*methoxybenzenesulphenanilide* (**10c**) (0.59 mmol, 42%), m.p. 82—84 °C; $\nu_{max.}$ 3 370 cm^{-1} (NH); *m/z* 339 (M^+), 230, 215, 199, 186, 110, and 109; δ 3.71 (3 H, s), 6.33—6.55 (2 H, m), 6.9—7.4 (10 H, m), and 7.6 (1 H, d, *J* 9 Hz) (Found: C, 67.05; H, 5.1; N, 4.2; S, 18.75. $C_{19}H_{17}NOS_2$ requires C, 67.2; H, 5.05; N, 4.15; S, 18.9%). A solution of (**10c**) (35 mg) in ether (30 ml) was shaken with 5 ml of 6M-hydrochloric acid for a few min and then the aqueous layer was separated, neutralized with 10% potassium carbonate, and extracted with ether. The combined organic layers were evaporated and the residue chromatographed to give the disulphide (**4**) and 5-methoxy-2-phenylthioaniline (**12**).

Continued elution gave (iii) an oily compound (**I**) (0.05 mmol, 4%), which probably was 3'-methoxy-2'-phenylthiobenzenesulphenanilide (**10a**) or the isomeric 3'-methoxy-4'-phenylthiobenzenesulphenanilide (**10b**); $\nu_{max.}$ 3 360 cm^{-1} (NH); *m/z* 339 (M^+), and 230; δ 3.82 (3 H, s), and 6.43—7.3 (13 H, m). Treatment of this compound (**I**) (20 mg) in ether with 6M-hydrochloric acid by the same procedure as just described for (**10c**) and subsequent evaporation of the organic phase gave a residue, which was dissolved in tetrahydrofuran (15 ml) and treated with a few drops of pentyl nitrite at 40 °C for 30 min. The resulting reaction mixture was analysed by t.l.c. (SiO_2) and g.l.c., which showed the presence of the disulphide (**4**) and 2-methoxyphenyl phenyl sulphide[17] as the main components.

Continued elution afforded (iv) 5'-*methoxy*-2',4'-*bis*(*phenylthio*)*benzenesulphenanilide* (**11**) (0.07 mmol, 7%), m.p. 119—120 °C; $\nu_{max.}$ 3 360 cm^{-1}; *m/z* 447 (M^+), 338, 337, 217, 109, and 108; δ 3.75 (3 H, s), 5.15 (1 H, br s), 6.55 (1 H, s), 7.0—7.3 (15 H,

m), and 7.65 (1 H, s) (Found: C, 67.25; H, 4.8; N, 3.1; S, 21.35. $C_{25}H_{21}NOS_3$ requires C, 67.1; H, 4.75; N, 3.15; S, 21.5%).

Further elution gave (v) unchanged (**1g**) (30%), (vi) 5-methoxy-2-phenylthioaniline (**12**) (0.055 mmol, 2%), and (vii) an oily compound (**II**) (0.13 mmol, 9%), which probably was (**10b**) or (**10a**); $\nu_{max.}$ 3 340 cm^{-1} (NH); *m/z* 339 (M^+) and 230; δ 3.7 (3 H, s), 5.3 (1 H, br s), and 6.2—7.4 (13 H, m). Treatment of this compound (**II**) with 6M-hydrochloric acid, and subsequent treatment with pentyl nitrite as described above for compound (**I**) led ultimately to a reaction mixture whose main components were the disulphide (**4**) and 2-methoxyphenyl phenyl sulphide,[17] as detected by t.l.c. (SiO_2) and g.l.c.

Final elution gave (viii) *m*-anisidine (**3g**) (0.62 mmol, 22%) and (ix) tarry material.

Decomposition of 3′-*Phenethylbenzenesulphenanilide* (**1h**) *with* 1.5 *Equiv. of TFA*.—Complete disappearance of starting (**1h**) occurred after *ca.* 1 h. Hydrolysis and then column chromatography gave (i) the disulphide (**4**) (1.50 mmol, 75%); (ii) a thick, red oil which probably was 2-*phenethyl*-N^2-*phenylthio*-N^1-(3-*dibenzylyl*)-p-*benzoquinone di-imine* (**8h**) (0.4 mmol, 20%); $\nu_{max.}$ 1 470, 1 310, and 1 160 cm^{-1}; *m/z* 498 (M^+), 496, 494, 479, 475, 392, 391, 387, and 301; δ 2.92 (4 H, s), 3.0 (4 H, s), and 6.55—7.55 (22 H, m) (Found: C, 80.6; H, 6.15; N, 5.5; S, 6.6. $C_{34}H_{30}N_2S$ requires C, 81.9; H, 6.05; N, 5.6; S, 6.45%); (iii) an unknown brown product (30 mg); (iv) a mixture of unidentified, coloured products (*ca.* 160 mg); and (v) 3-aminobibenzyl (**3h**) (1.68 mmol, 42%). Continued elution afforded tarry material.

Decomposition of 2′-*Phenylbenzenesulphenanilide* (**1i**) *with* 1.5 *Equiv. of TFA*.—Disappearance of the starting material (**1i**) was complete after *ca.* 1 h. Hydrolysis and then chromatography furnished (i) the disulphide (**4**) (1.56 mmol, 78%); (ii) an orange, thick oil, which probably was 2-*phenyl*-N^2-(*biphenyl*-2-*yl*)-N^1-*phenylthio*-p-*benzoquinone di-imine* (**8i**) (0.36 mmol, 18%), $\nu_{max.}$ 1 490 and 700 cm^{-1}; *m/z* 442 (M^+), 385, 333, 218, 167, and 109 (Found: C, 80.4; H, 5.15; N, 6.9; S, 6.85. $C_{30}H_{22}N_2S$ requires C, 81.4; H, 5.0; N, 6.55; S, 7.15%); (iii) a mixture of two unidentified products (50 mg); (iv) 2-aminobiphenyl (**3i**) (2.1 mmol, 52%); and (v) tarry material.

Decomposition of N-(p-*Methoxyphenyl*)*bis*(*benzenesulphen*)*amide* (**6a**).—(a) *With* 1.5 *equiv. of TFA*. Hydrolysis (after 10 min) and then column chromatography gave (i) the disulphide (**4**) (3 mmol, 75%); (ii) the *p*-quinone di-imine (**8a**) (0.9 mmol, 46%); (iii) *p*-anisidine (**3a**) (0.43 mmol, 11%); and (iv) the phenazine (**9a**) (0.14 mmol, 7%).

(b) *With* 3 *equiv. of TFA in the presence of* p-*toluidine* (**3b**) (2 *equiv.*). Hydrolysis (after 10 min) and then chromatography gave (i) diphenyl disulphide (**4**) (2.02 mmol, 59%); (ii) unchanged (**6a**) (0.6 mmol, 15%); (iii) N-(p-*tolyl*)-N-*phenylthio*-p-*benzoquinone di-imine* (**8b**) (0.95 mmol, 28%), m.p. 143—144 °C; $\nu_{max.}$ 1 495, 1 475, 1 315, and 1 105 cm^{-1}; *m/z* 304 (M^+), 195, 169, 110, 109, and 91; δ 2.33 (3 H, s) and 6.7—7.7 (13 H, m) (Found: C, 74.7; H, 5.25; N, 9.15; S, 10.7. $C_{19}H_{16}N_2S$ requires C, 75.0; H, 5.3; N, 9.2; S, 10.55%); (iv) 4′-methylbenzenesulphenanilide (**1b**) (0.63 mmol, 19%); (v) *N*-(*p*-methoxyphenyl)-*N*′-phenylthio-*p*-benzoquinone di-imine (**8a**) (0.22 mmol, 13%); (vi) *p*-toluidine (**3b**); (vii) *p*-anisidine (**3a**) (0.68 mmol, 20%). Quantitative g.l.c. analysis of an aliquot of the reaction mixture gave 2,7-dimethoxyphenazine (**9a**) (0.04 mmol, 2%).

Decomposition of N-(p-*Tolyl*)*bis*(*benzenesulphen*)*amide* (**6b**) *with* 3 *Equiv. of TFA in the Presence of* p-*Anisidine* (**3a**) (2 *Equiv.*).—Hydrolysis (after 10 min) and then column chromatography gave (i) the disulphide (**4**) (2.83 mmol, 83%); (ii) unchanged (**6b**) (0.60 mmol, 15%); (iii) 4′-methylbenzenesulphenanilide (**1b**) (0.31 mmol, 9%); (iv) 4′-methoxybenzenesulphenanilide (**1a**) (0.1 mmol, 3%); (v) a mixture of unidentified products (30 mg) probably containing also trace amounts of the *p*-quinone di-imines (**8a**) and (**8b**); (vi) 2,7-dimethylphenazine (**9b**) (0.42 mmol, 25%); (vii) 2-methoxy-7-methylphenazine (0.51 mmol, 15%); *m/z* 224 (M^+), 209, and 181; δ 2.6 (3 H, s), 4.0 (3 H, s), and 7.2—8.0 (6 H, m); (viii) *p*-toluidine (**3b**) (1.0 mmol, 29%); and (ix) *p*-anisidine (**3a**).

Decomposition of N-*Phenylbis*(*benzenesulphen*)*amide* (**6c**) *with* 1.5 *Equiv. of TFA*.—Hydrolysis (after 10 min) and chromatography gave (i) the disulphide (**4**) (2.75 mmol, 76%); (ii) starting material (**6c**) (0.39 mmol, 5%); (iii) the benzenesulphenanilide (**1c**) (0.36 mmol, 10%); (iv) the *p*-benzoquinone di-imine (**8c**) (0.36 mmol, 20%); (v) the phenazine (**9c**) (0.055 mmol, 3%); (vi) aniline (**3c**) (0.80 mmol, 22%); (vii) an unknown violet product (30 mg); and (viii) tarry material.

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