Benzenesulphenanilidyl Radicals. Part 3.[1] Reactions of 4'-Substituted Benzenesulphenanilides with t-Butoxyl Radicals

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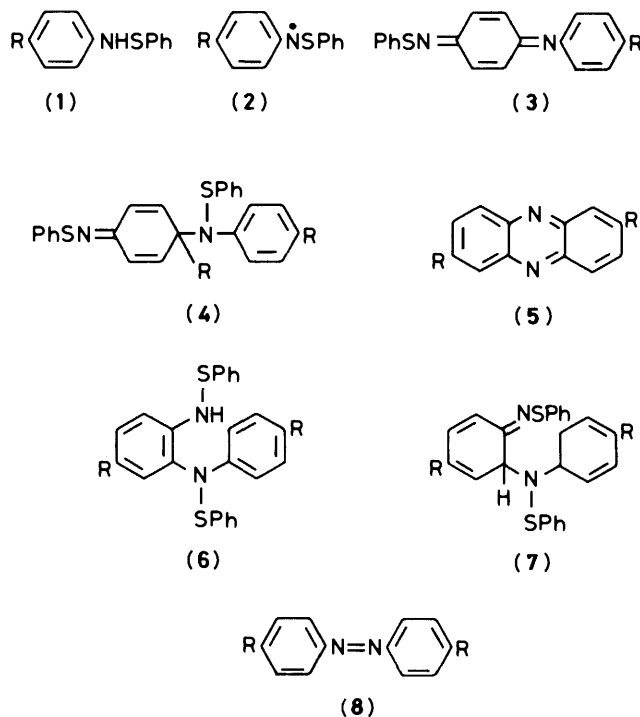*Istituto di Chimica Organica dell'Università, Via le Risorgimento 4, 40136 Bologna, Italy*

Decomposition products of the 4'-substituted benzenesulphenanilidyl radicals (2a, b, d, and e), generated from the corresponding benzenesulphenanilides (1) with t-butoxyl radicals, have been investigated in benzene, acetonitrile, and acetone. Results indicate that the decomposition modes exhibited by these radicals are not essentially influenced by variation of the solvent polarity; comparison of the findings with present and previous results from the oxidation of (1) with lead dioxide show that the chemical reactivity trend displaced by the thioaminyls (2) can be greatly influenced both by the reaction medium and the 4'-substituent. Evidence is presented that the benzenesulphenanilides (1b) and (1e) react in acetone in the presence of di-t-butyl hyponitrite to give products ascribable to homolytic substitution at the sulphenanilide sulphur by acetonyl radicals.

In two previous papers [1,2] we have reported our results from an investigation of the chemical reactivity of a number of 4'-substituted benzenesulphenanilidyl radicals (2a—e), generated by oxidation, with lead dioxide, of the corresponding benzenesulphenanilides. These radicals were found to exhibit chemical behaviour which may largely depend both on the nature of the 4'-substituent and on the polarity of the reaction solvent employed. In fact, the oxidation of the sulphenanilides (1a—c) [1] in benzene led to the formation of the *p*-benzoquinone di-imines (3a—c), arising from *p*-C–N coupling of radicals (2a—c) and subsequent fragmentation of the ensuing dimers (4a—c), whereas the 4'-methoxy- and 4'-nitro-benzenesulphenanilides (1d) [2] and (1e) [1] gave the phenazine (5d) and the *o*-phenylenediamine (6e), respectively, as the final products resulting from the *o*-C–N dimers (7) of the corresponding radicals (2d) and (2e). Moreover the apparent chemical trend displayed by radicals (2b), (2c), and (2e) was found to change drastically when they were produced in acetonitrile, whilst the chemical reactivity of the parent radicals (2a) was found to remain virtually unchanged. In this solvent, the oxidation of sulphenanilides (1b) and (1c) showed smooth formation of the phenazines (5b) and (5c) at the expense of the di-imines (3b and c).[1] On the other hand, in acetonitrile (and acetone) the 4'-nitrobenzenesulphenanilide (1e) afforded the azobenzene (8e) in fairly high to high yields as the only product ascribable to dimerization of radicals (2e).[1] Results obtained in acetonitrile (and acetone) were discussed in terms of a possible mechanism involving effective oxidation by lead dioxide of N–N dimers assumed to be in rapid equilibrium with the corresponding sulphenanilidyl radicals (2b, c, e).

In this paper we report our study of the reactions of the 4'-substituted benzenesulphenanilides (1a, b, d, and e) with di-t-butyl hyponitrite (DBH), performed at 40 °C in benzene, acetonitrile, and acetone. This study was carried out in order to compare the chemical reactivity trend displayed by the thio-aminyls (2a, b, d, and e), generated from anilides (1) with t-butoxyl radicals, with that previously observed from the related oxidation of compounds (1) with lead dioxide. In fact, it was of interest to us to ascertain whether and to what extent the lead dioxide might play a role in affecting the chemical reactivity patterns of radicals (2), thus disclosing the actual substituent and solvent effects on their reactivity.

(1)   (2)   (3)

(4)

(5)

(6)

(7)

(8)

a ; R = H   c ; R = Br   e ; R = NO₂
b ; R = Cl   d ; R = OMe

formation of diphenyl disulphide (9) (19%), *NN*-bis(phenylthio)-*p*-anisidine (10d) (51%) ascribable to coupling of radical (2d) with phenylthio radicals,[2] and the phenazine (5d) (45%), the final product resulting from *o*-C–N dimerization of radical (2d),[2] as well as *N*-(*p*-methoxyphenyl)-*N*'-phenylthio-*p*-benzo-quinone di-imine (3d) (28%); the same products were isolated in comparable yields when the reaction was carried out in acetone
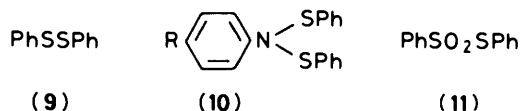
Results and Discussion

Thermal decomposition of DBH in benzene solution in the presence of 4'-methoxybenzenesulphenanilide (1d) led to the

PhSSPh   (10)   PhSO₂SPh

(9)   (10)   (11)

Table. Product yields[a] for the reaction of benzenesulphenanilides (1) with DBH at 40 °C and with lead dioxide at room temperature

Benzene-sulphenanilide	Conditions	Products (%)									
		(3)	(5)	(6)	(8)	(9)	(10)	(11)	(13)	(14)	(15)
(1a)	PbO₂, C₆H₆[b]	40				10	8				
	PbO₂, MeCN	73				21					
	DBH, C₆H₆	73				24	25				
	DBH, acetone	55				22	7	9			
(1b)	PbO₂, C₆H₆[b]	65	1			22	9	22			
	PbO₂, MeCN[b]		64			44					
	DBH, C₆H₆	d	15			35	3	31			
	DBH, MeCN	35	24			42	4				
	DBH, acetone					29				38[e]	43[e]
(1d)	PbO₂, C₆H₆[c]		34			9	80				
	PbO₂, MeCN		75			59	20				
	DBH, C₆H₆	28	45			19	51				
	DBH, acetone	17	57			16	42	7			
(1e)	PbO₂, C₆H₆[b]			22	2	5		33			
	PbO₂, MeCN[b]				73	73					
	PbO₂, acetone[b]				90	91					
	DBH, C₆H₆		10		1	11		17	26[e]	12[e]	
	DBH, acetone					26				30[e]	35[e]

[a] Yields are based on 2 mol of (1) giving 1 mol each of the products, unless otherwise noted. [b] From ref. 1. [c] From ref. 2. [d] The di-imine (3b) was not isolated, see text. [e] Yields based on 1 mol of (1) giving 1 mol of the product.

(Table). Moreover, a similar trend was observed in acetonitrile, as shown by a qualitative experiment.

The hitherto unknown di-imine (3d), which could be identified on the basis of elemental analysis and spectral and chemical evidence, clearly is the product formed through p-C-N dimerization of radical (2d) and subsequent fragmentation of the ensuing dimer (4d). Thus, these results indicate that the radical (2d) can undergo p-C-N coupling in competition with o-C-N coupling, the chemical trend exhibited by radical (2d) being not essentially affected by variation of the solvent polarity. Furthermore, these findings are consistent with those we previously reported[2] for the related reaction of the anilide (1d) with di-t-butyl peroxide in refluxing benzene, except that no evidence of formation of the di-imine (3d) was provided since this compound had not been identified; our subsequent re-investigation of the reaction, which has been carried out in the light of the above results, has led us to establish that the di-imine (3d) is actually formed in a yield comparable with that of the phenazine (5d) (30 and 34%, respectively).

The di-imine (3d) is not formed in the oxidation of the anilide (1d) with lead dioxide either in benzene, as previously reported,[2] or in acetonitrile, as found in the present work, the only remarkable difference on passing from benzene to acetonitrile being a noticeable increase in the yields of the phenazine (5d) and the disulphide (9) at the expense of the p-anisidine (10d) (Table).

On the other hand, we have previously shown[2] that thio-aminyl (2d) can also be produced by thermal decomposition of the NN-bis(phenylthio)-p-anisidine (10d) in refluxing benzene; under these conditions the decomposition of radicals (2d) was reported to afford the phenazine (5d) as the exclusive product ascribable to dimerization of these radicals; substantial confirmation of such a trend has been obtained from a repeat experiment performed in the present work, which showed the formation of phenazine (5d) (55%) to be accompanied only by very small amounts of the p-quinone di-imine (3d) (3%).

On the basis of all our evidence of the chemical reactivity of radicals (2d) it should be inferred that p-C-N dimerization leading to dimer (4d) competes with o-C-N coupling to afford isomer (7d) although it would appear that fragmentation of the dimer (4d) to the di-imine (3d) can effectively occur only in the presence of t-butoxyl radicals.
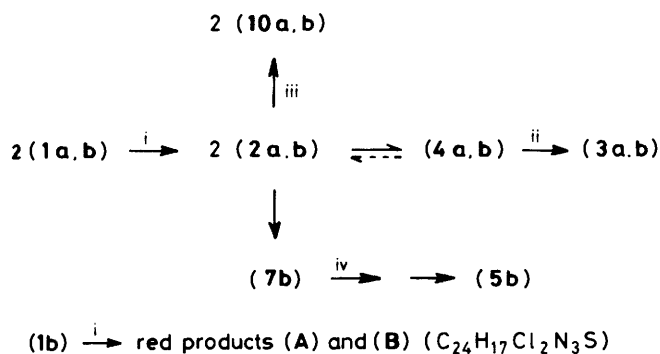
In the absence of t-butoxyl radicals, fragmentation [leading to the original radicals (2d)] would be the main (if not exclusive) route opened to dimer (4d), as also evidenced by the fact both in the oxidation of sulphenanilide (1d) and in the thermolysis of the aniline (10d) that the overall yields of identifiable products are generally very high. A possible role played by t-butoxyl radicals in favouring the fragmentation of dimer (4d) to di-imine (3d) might be its assistance in the formal elimination of PhSOMe through hydrogen abstraction from the methoxy group leading, with concomitant loss of formaldehyde, to the resonance-stabilized aminyl radical (12). Subsequent loss of phenylthio radical from (12) would then afford the di-imine (3d) (Scheme 1).
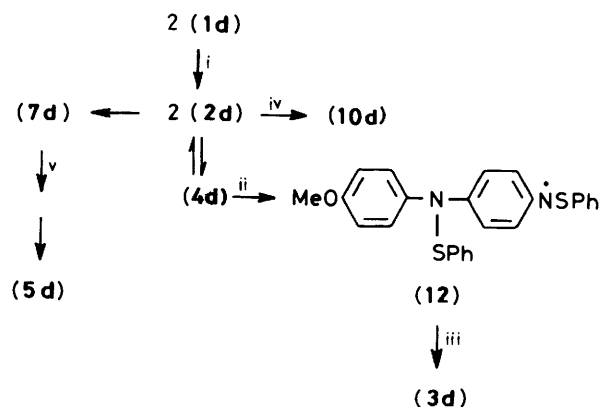
Scheme 1. *Reagents and conditions:* i, DBH–benzene (or acetone, MeCN), 40 °C; or (t-BuO)₂–benzene, 80 °C; ii, t-BuO˙, −t-BuOH, −HCHO; iii, −PhS˙; iv, 2PhS˙; v, −2PhSH

The evidence concerning the chemical reactivity of the parent sulphenanilidyl radicals (2a), which was obtained from the reaction of the anilide (1a) with DBH, was in full agreement with that provided by the oxidation of compound (1a) with lead dioxide (Table). In fact, the reaction, carried out both in benzene and in acetone, in both cases led to the isolation of the p-benzoquinone di-imine (3a) in fairly high yields in addition to

the disulphide (9) and the aniline (10a); formation of some S-phenyl benzenethiosulphonate (11), the source of which is unknown, also occurred in acetone (Table). Thus, it may be concluded that the parent thioaminyl (2a), largely irrespective of the reaction conditions, undergoes p-C–N coupling as the most preferred (if not exclusive) dimerization mode (Scheme 2).

2 (10a, b)

↑ iii

2 (1a, b) ⟶ⁱ 2 (2a, b) ⇌ (4a, b) ⟶ⁱⁱ (3a, b)

↓

(7b) ⟶ⁱᵛ ⟶ (5b)

(1b) ⟶ⁱ red products (A) and (B) (C₂₄H₁₇Cl₂N₃S)

Scheme 2. *Reagents and conditions:* i, DBH–benzene or acetone [(1a)] {or MeCN [(1b)]}, 40 °C; ii, −PhSH or −PhSCl; iii, 2PhS·; iv, −2PhSH

The reaction of the 4′-chlorobenzenesulphenanilide (1b) with DBH in benzene afforded 4-chloro-NN-bis(phenylthio)aniline (10b) (3%), 2,7-dichlorophenazine (5b) (15%), diphenyl disulphide (9) (35%), the thiosulphonate (11)¹ (31%), and an unknown reddish product (A) together with an unidentified red compound (B) (32%). The i.r. spectrum of compound (B) showed NH stretching absorptions at 3 350 cm⁻¹; elemental analysis and the parent ion in the mass spectrum were consistent with the molecular formula $C_{24}H_{17}Cl_2N_3S$, thus pointing to a product apparently derived from 4′-chlorobenzenesulphen-anilide addition to the p-benzoquinone di-imine (3b), followed by loss of thiophenol. In fact, the di-imine (3b), which was the product expected¹ from p-C–N dimerization of radical (2b), was not isolated, but control experiments clearly showed that di-imine (3b) was initially formed as a major product and that it subsequently disappeared to give the unknown compounds (A) and (B). The same reaction, carried out in acetonitrile, afforded the disulphide (9) (42%), the 4-chloroaniline (10b) (4%), the di-imine (3b) (35%), and the phenazine (5b) (24%) (Scheme 2).

A similar trend was exhibited by radical (2b) when produced by thermolysis, at 55 °C, of p-chloro-NN-bis(phenylthio)aniline (10b) in benzene solution; in fact, the reaction mixture led to the isolation of the disulphide (9) (49%), the thiosulphonate (11) (22%), and the benzenesulphenanilide (1b) (the hydrogen-abstraction product, 26%) in addition to the phenazine (5b) (15%) and a mixture of unidentified coloured products. Also in this case, the di-imine (3b) was not isolated, but t.l.c. analysis clearly showed that the initially formed di-imine (3b) was not capable of surviving the reaction conditions, but gave rise to a number of unknown decomposition products.

These results, while indicating that the chemical behaviour of the radical (2b) is not essentially influenced by varying the solvent polarity, would also suggest that o-C–N coupling leading to dimer (7b) and p-C–N coupling giving dimer (4b) can occur to a comparable extent; furthermore, it would appear that fragmentation of the p-C–N dimer (4b) to give di-imine (3b) should not be largely affected by the presence of t-butoxyl radicals. On the other hand the above findings, as compared with those we previously obtained¹ from the oxidation of compound (1b) with lead dioxide in benzene (Table), would suggest that p-C–N dimerization of radical (2b) should be reversible and kinetically preferred over o-C–N dimerization in

view of the almost exclusive formation of the di-imine (3b) at the expense of the phenazine (5b) when the oxidation of compound (1b) is performed in benzene; this suggestion is based on the assumption that free thioaminyl (2b) is actually involved in the oxidation of the anilide (1b) with lead dioxide in benzene, in line with the general evidence provided by earlier e.s.r. studies.³ In such a case, lead dioxide might effectively aid in the conversion of the dimer (4b) into di-imine (3b), thus removing dimer (4b) from its equilibrium with radical (2b), presumably by promoting the elimination of PhSCl through preliminary co-ordination with the cyclohexadienyl halogen atom. Support for such mechanistic interpretation comes from our results from the oxidation of anilide (1b) with silver(I) oxide in benzene, which gave the p-benzoquinone di-imine (3b) in 95% yield in addition to the disulphide (9) and the aniline (10b). These findings, while being in full agreement with those we previously reported for the related oxidation of 4′-bromobenzenesulphenanilide (1c) with silver(I) oxide,¹ are also in line with the reasonable expectation that silver(I) oxide should be more effective than lead dioxide in promoting halide removal from (4b), thus causing a more feasible fragmentation of (4b) to di-imine (3b).

On the basis of the available evidence concerning the re-activity of the radical (2b), our earlier findings¹ that exclusive formation of the phenazine (5b) at the expense of the di-imine (3b) occurs in the oxidation of compound (1b) with lead dioxide in acetonitrile (Table) are not readily explained in terms of a route involving o-C–N dimerization of free thioaminyl (2b). On this basis, the mechanism involving oxidation of initially formed N–N dimers of radical (2b), which we previously postulated to explain the formation of phenazine (5b) in acetonitrile, remains conceivable.¹ However, the possibility that the trend observed in such a polar solvent might be essentially ascribable to surface effects, causing dimerization of thioaminyl (2b) bound in some way to the oxidant, should not be ruled out.

The reaction of the 4′-nitrobenzenesulphenanilide (1e) with DBH in benzene led to a complex reaction mixture, from which the disulphide (9) (11%), the phenazine (5e) (10%), the benzenethiosulphonate (11) (17%), 4,4′-dinitroazobenzene (8e) (1%), the t-butyl benzenesulphinate (13) (26%), and 4-nitro-aniline (14e) (12%) could be isolated as the only identifiable products (Scheme 3).

PhSOBuᵗ R⟨ ⟩NH₂ PhSCH₂CCH₃
‖   ‖
O   O

(13)   (14)   (15)
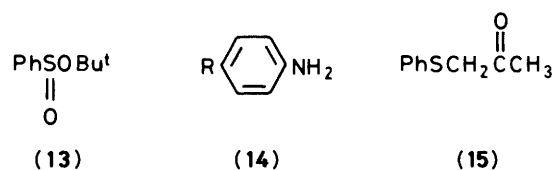
These findings are comparable to our earlier ones¹ obtained for the oxidation of anilide (1e) with lead dioxide in benzene, which analogously led to a complex reaction mixture, from which compounds (9), (8e), and (11) were isolated in similar yields, in addition to the o-diamine (6e), the likely precursor of the phenazine (5e) (Table).

As for the benzenesulphinate (13), its formation in con-siderable amounts is noteworthy, but why it is formed is unclear at present as is the actual source of the thiosulphonate (11); however, the concomitant presence of compounds (11) and (13) might possibly suggest intermediate occurrence of phenyl benzenethiosulphinate [PhS(O)SPh]; in fact, PhS(O)SPh might disproportionate⁴ to give the thiosulphonate (11) [and (9)], and undergo nucleophilic attack by t-butyl alcohol, presumably present in the reaction medium, to give the benzenesulphinate (13).⁴,⁵ As for the occurrence of the aniline (14e), the findings obtained from the same reaction carried out in acetone (see later) would suggest that some radical dis-
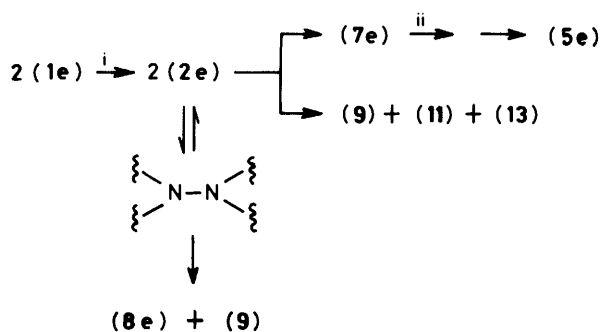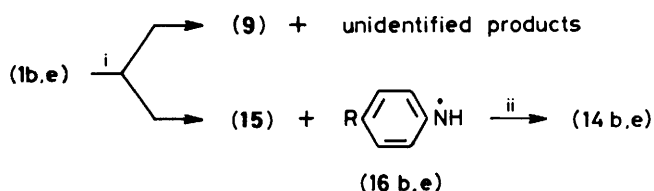
Scheme 3. *Reagents and conditions:* i, DBH–benzene or MeCN, 40 °C; ii, −2PhSH

placement at the sulphur of anilide (1e) might possibly be responsible for its formation.

The reaction of the sulphenanilide (1e) with DBH was found not to exhibit any significant change when carried out in acetonitrile, as shown by a qualitative experiment.

Therefore, it may be inferred that the chemical trend exhibited by the thioaminyl radical (2e) is not significantly affected by variation of the solvent polarity. Thus, the exclusive formation of the azobenzene (8e) [and (9)] previously observed[1] in the oxidation of compound (1e) with lead dioxide in acetonitrile (and acetone) can reasonably be explained in terms of a primary role played by the oxidant in affecting the decomposition of radical (2e) in these polar solvents, in line with our earlier suggestion.[1]

Surprisingly, the reactions of anilides (1e) and (1b) with DBH in acetone did not provide any evidence of products ascribable to the radicals (2e) and (2b); in fact, these reactions afforded the disulphide (9) (26—29%), the anilines (14e) and (14b) (30—38%), and (phenylthio)acetone (15) (35—43%) together with a number of unidentifiable products. Thus, it would seem that radical displacement at the sulphur atom by acetonyl radicals is the predominant reaction path undergone by the benzene-sulphenanilides (1b) and (1e) under these conditions. The formation of comparable amounts of compound (15) and the substituted anilines (14b) and (14e), respectively, may be reasonably explained in terms of homolytic substitution at the sulphur of anilides (1b) and (1e) by acetonyl radicals, leading to compound (15) and the corresponding anilino radicals (16b, and e), from which the anilines (14b) and (14e) would result by hydrogen abstraction; however, the source of the disulphide (9) isolated from these reactions is unknown (Scheme 4).

Scheme 4. *Reagents and conditions:* i, DBH–acetone, 40 °C; ii, RH, −R·

Radical substitution at sulphur (S_H2 reaction) in a variety of sulphur compounds is well documented,[6] but to our knowledge no examples of S_H2 reaction at the sulphenamide sulphur have been reported so far. Since we have observed that sulphen-anilides (1a) and (1d) smoothly afford the corresponding radicals (2a) and (2d) by reaction with DBH in acetone, the radical displacement at sulphur occurring with the anilides (1b)

and (1e) should be essentially ascribed to the effects of the electron-attracting chloro- and nitro-substituent, and this is possibly related to the formation of strong hydrogen bonds between the sulphenanilides (1b) and (1e) and the solvent, which would make the hydrogen abstraction from these compounds much less feasible; sulphenanilides (1b) and (1e) would therefore undergo radical attack at the sulphur atom by the acetonyl radicals, effectively produced at the expense of the t-butoxyl radicals, much more readily than hydrogen abstraction, thus leading to the corresponding thioaminyls (2b) and (2e).

On the basis of our present results from the study of the reactivity of 4′-substituted benzenesulphenanilidyl radicals (2) produced from anilides (1) by hydrogen abstraction with t-butoxyl radicals, it may be inferred that the chemical behaviour of these radicals is generally unaffected by solvent polarity.

Moreover, these findings, in addition to those presently and previously reported for the thioaminyls (2) produced by oxidation of compounds (1) with lead dioxide and by thermolysis of anilines (10), lead to the conclusion that the decomposition modes undergone by these radicals can be greatly influenced by the nature of the 4′-substituent and by the reaction medium employed.

Experimental

The benzenesulphenanilides (1a), (1b), (1d), and (1e) were prepared as previously described.[1,2] Reaction products, such as diphenyl disulphide (9),[1] *s*-phenyl benzenethiosulphonate (11),[1] the phenazines (5b),[1] (5d),[2] and (5e),[1] and the *p*-benzoquinone di-imines (3a) and (3b),[1] 4,4′-dinitroazobenzene (8e),[1] the bis(phenylthio)anilines (10a), (10b), and (10d),[1] and (phenyl-thio)acetone (15),[7] were each identified by spectral comparison with authentic specimens. Column chromatography was carried out on Merck silica gel (0.040—0.063 particle size), using light petroleum (b.p. 40—60 °C) with increasing amounts of diethyl ether (up to 90%) as eluant. Oxidation of the benzene-sulphenanilides (1a) and (1d) with lead dioxide in acetonitrile and of (1b) with silver(I) oxide in benzene was carried out according to the general procedure described in part 2,[1] [from 2 mmol of the sulphenanilide (1a, b, or d) and lead dioxide (10 g) or silver(I) oxide (4g) in 150 ml of the appropriate solvent (reaction times *ca.* 24—48 h)]. Yields of identified products from the oxidation of compounds (1a) and (1d) with lead dioxide and from the reaction of sulphenanilides (1a), (1b), (1d), and (1e) with DBH are calculated from consumed starting benzenesulphenanilide (1) and are given in the Table.

Oxidation of Benzenesulphenanilide (1a) with Lead Dioxide in Acetonitrile.—Column chromatography afforded (i) the di-sulphide (9); (ii) *N*-phenyl-*N*′-phenylthio-*p*-benzoquinone di-imine (3a); (iii) a mixture of unidentified products (50 mg); and (iv) an unknown, red compound (55 mg).

Oxidation of 4′-Methoxybenzenesulphenanilide (1d) with Lead Dioxide in Acetonitrile.—The reaction mixture from the oxidation of compound (1d), after filtration of the lead dioxide, was refluxed for *ca.* 15 min [to bring about complete formation of the phenazine (5d) from its precursor][2] and then chromatographed to give (i) the disulphide (9); (ii) the *p*-anisidine (10d); and (iii) 2,7-dimethoxyphenazine (5d).

Oxidation of 4′-Chlorobenzenesulphenanilide (1b) with Silver(I) Oxide in Benzene.—Column chromatography afforded (i) the disulphide (9) (0.033 g, 15%); (ii) the aniline (10b) (0.017 g, 5%); (iii) the *p*-benzoquinone di-imine (3b) (0.308 g, 95%); and (iv) the phenazine (5b) (0.003 g, 1%).

Reaction of Benzenesulphenanilides (**1**) *with Di-t-butyl Hyponitrite. General Procedure.*—To a solution of the benzenesulphenanilide (**1a, b, d,** or **e**) (1 mmol) in the appropriate solvent (15 ml) was added di-t-butyl hyponitrite[8] (1.2 mmol) and the resulting mixture was kept at 40 °C for *ca.* 48 h. The excess of solvent was distilled off and the residue was chromatographed on a silica gel column.

Reaction of the Anilide (**1a**) *with DBH.*—(a) *In benzene.* Chromatography gave (i) the disulphide (**9**); (ii) *NN*-bis-(phenylthio)aniline (**10a**); (iii) the starting material (**1a**) (10%); an unidentified product (7 mg); (iv) the *p*-benzoquinone di-imine (**3a**); and (v) an unknown, violet compound (11 mg).

(b) *In acetone.* Chromatography afforded (i) the disulphide (**9**); (ii) the aniline (**10a**); (iii) unchanged (**1a**) (8%); (iv) the benzenethiosulphonate (**11**); (v) the di-imine (**3a**); and (vi) a mixture of two unidentified products (10 mg).

Reaction of the Anilide (**1b**) *with DBH.*—(a) *In benzene.* Chromatography gave (i) the disulphide (**9**); (ii) 4-chloro-*NN*-bis(phenylthio)aniline (**10b**); (iii) the phenazine (**5b**); (iv) an unidentified red compound (**B**) (32%), m.p. 153—155 °C; $v_{max.}(CS_2)$ 3 350 cm^{-1} (NH); m/z 449 (M^+), 414, 378, 335, 321, and 303 (Found: C, 64.15; H, 3.7; Cl, 15.1; N, 9.3; S, 6.95. $C_{24}H_{17}Cl_2N_3S$ requires C, 64.0; H, 3.8; Cl, 15.75; N, 9.35; S, 7.1%); (v) the benzenethiosulphonate (**11**); and (vi) an unknown reddish product (**A**) (15 mg), m/z 447 (M^+).

(b) *In acetonitrile.* Chromatography gave (i) the disulphide (**9**); (ii) the aniline (**10b**); (iii) the phenazine (**5b**); (iv) unchanged (**1b**) (20%); (v) the *p*-benzoquinone di-imine (**3b**); (vi) a mixture of unidentified products (15 mg).

(c) *In acetone.* Chromatography afforded (i) the disulphide (**9**); (ii) (phenylthio)acetone (**15**); (iii) a mixture of unidentified products (20 mg); (iv) 4-chloroaniline (**14b**), identical in all respects with a commercial sample; and (v) tarry material.

Reaction of the Anilide (**1d**) *with DBH.*—(a) *In benzene.* Chromatography gave (i) the disulphide (**9**); (ii) the *p*-anisidine (**10d**); (iii) the starting material (**1d**) (5%); (iv) N-(*p-methoxyphenyl*)-N'-*phenylthio-p-benzoquinone di-imine* (**3d**), m.p. 150—152 °C; $v_{max.}(CCl_4)$ 2 850, 1 510, and 1 250 cm^{-1}; $v_{max.}(CS_2)$ 840, 745, 725, and 695 cm^{-1}; m/z 320 (M^+), 305, 218, 214, 213, 212, 211, 199, 198, 197, 185, 168, 110, and 109; $\delta(CDCl_3)$ 3.8 (3 H, s) and 6.8—7.75 (13 H, m) (Found: C, 71.55; H, 5.0; N, 8.65; S, 9.85. $C_{19}H_{16}N_2OS$ requires C, 71.2; H, 5.05; N, 8.75; S, 10.0%); reduction of (**3d**) (100 mg) in tetrahydrofuran (40 ml) with a 30% aqueous solution of sodium dithionite by a procedure analogous to that previously described[1] for the di-imines (**3a** and **b**) gave N-(*p*-methoxyphenyl)-*p*-phenylenediamine (40%), identical in all respects with an authentic commercial sample; and (v) the phenazine (**5d**).

(b) *In acetone.* Chromatography afforded (i) the disulphide (**9**); (ii) the *p*-anisidine (**10d**); (iii) the starting material (**1d**) (12%); (iv) the benzenethiosulphonate (**11**); (v) a mixture of unidentified products (20 mg); (vi) the di-imine (**3d**); and (vii) the phenazine (**5d**).

Reaction of the Anilide (**1e**) *with DBH.*—(a) *In benzene.* Chromatography gave (i) the disulphide (**9**); (ii) 4,4'-dinitro-azobenzene (**8e**); (iii) the benzenethiosulphonate (**11**); (iv) t-butyl benzenesulphinate (**13**),[9] m/z 198 (M^+), 143, 125, 97, 77, and

57; $\delta(CDCl_3)$ 1.5 (9 H, s) and 7.4—7.7 (5 H, m); (v) unchnaged (**1e**) (15%); (vi) 2,7-dinitrophenazine (**5e**); and (vii) 4-nitroaniline (**14e**), identical in all respects to a commercial sample.

(b) *In acetone.* Chromatography gave (i) the disulphide (**9**); (ii) (phenylthio)acetone (**15**); (iii) the starting material (**1e**) (10%); (iv) a mixture of unidentified products (30 mg); (v) 4-nitroaniline (**14e**); and (vi) tarry material.

Reaction of the Anilide (**1d**) *with Di-t-butyl Peroxide.*—This reaction was carried out as described in Part 1[2] with compound (**1d**) (0.72 g, 3.12 mmol). Column chromatography gave (i) the disulphide (**9**) (0.033 g, 12%); (ii) the *p*-anisidine (**10d**) (0.28 g, 65%); (iii) unchanged (**1d**) (0.13 g, 18%); (iv) the di-imine (**3d**) (0.124 g, 30%); and (v) the phenazine (**5d**) (0.104 g, 34%).

Thermal Decomposition of the Anisidine (**10d**).—This was performed as described in Part 1[2] with compound (**10d**) (0.85 g, 2.51 mmol). Column chromatography gave (i) the disulphide (**9**) (0.217 g, 74%); (ii) the starting material (**10d**) (0.39 g, 46%); (iii) the anilide (**1d**) (0.125 g, 40%); (iv) the di-imine (**3d**) (0.007 g, 3%); and (v) the phenazine (**5d**) (0.090 g, 55%).

Thermal Decomposition of the Aniline (**10b**).—This was performed with compound (**10b**) (0.345 g, 1 mmol) in benzene (75 ml) at 55 °C (*ca.* 120 h). Column chromatography gave (i) the disulphide (**9**) (0.095 g, 49%); (ii) the starting material (**10b**) (0.038 g, 11%); (iii) the anilide (**1b**) (0.055 g, 26%); (iv) the phenazine (**5b**) (0.017 g, 15%); (v) the thiosulphonate (**11**) (0.050 g, 22%); and (vi) a mixture of unidentified products (0.030 g).

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