

Benzenesulphenanilidyl Radicals. Part 2.¹ Substituent and Solvent Effects on the Reactivity of 4'-Substituted Benzenesulphenanilidyl Radicals Produced by Oxidation with Lead Dioxide of the Corresponding Benzenesulphenanilides

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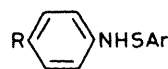
Oxidation of benzenesulphenanilide (1d) with lead dioxide in benzene affords the *p*-benzoquinone diimine (5d) together with minor amounts of *N,N*-bis(phenylthio)aniline (4d) and diphenyl disulphide (7a). The formation of the products is explained in terms of *p*-C-N coupling of the benzenesulphenanilidyl radicals (2d) and subsequent fragmentation of the resulting dimer. A similar trend is observed in the oxidation of 4'-chloro- and 4'-bromo-benzenesulphenanilides (1e) and (1f), whereas 4'-nitrobenzenesulphenanilide (1g) leads to the *o*-phenylenediamine (12g), arising from *o*-C-N coupling of the sulphenanilidyl radical (2g). The oxidation of the sulphenanilides (1e) and (1f) in acetonitrile produces the phenazines (3e) and (3f) and the disulphide (7a), whereas the anilide (1g) and 4'-cyanobenzenesulphenanilide (1h) give azobenzenes (11g) and (11h) and the disulphide (7a); these results are discussed in terms of a possible mechanism involving oxidation of the N-N dimers (14e-h) which are in rapid equilibrium with the corresponding sulphenanilidyl radicals (2e-h). Evidence is also presented that the oxidation of 2-nitrobenzenesulphenanilides leads to products ascribable to intermediate 2-nitrobenzenesulphenanilidyl radicals, in contrast with a previous claim.

In the last few years a large variety of benzenesulphenanilidyl radicals (2), a new family of arylaminyl radicals bearing a sulphur atom adjacent to the radical centre, have been produced and an extensive e.s.r. spectroscopic investigation has been carried out.² E.s.r. results have shown that the thioaminyls (2) are fairly stable radicals, which have been proved to be long-lived if sterically protected. In fact, a number of sterically protected thioaminyls (2) have been isolated as pure crystals^{2d} or, at low temperature, as N-N dimers [these dissociate at room temperature to give back the radicals (2)].^{2c}

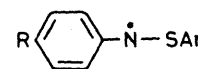
The chemistry of these radicals is not well known; the only available data are from the decomposition of 4-chloro-3',5'-di-*t*-butylbenzenesulphenanilidyl radicals,³ generated from the N-N dimers in benzene solution, which were found to undergo hydrogen abstraction and *o*-C-N dimerization as major reactions, and from our recent report¹ on the reactivity of 4'-methoxy- and 4'-methoxy-2-nitro-benzenesulphenanilidyl radicals (2a) and (2c), which were produced in benzene from the benzenesulphenanilides (1a) and (1c) by reaction with *t*-butoxy radicals or oxidation with lead dioxide.

In this latter paper we showed that the radicals (2a) undergo *o*-C-N coupling to give the dimers (13a), from which the phenazine (3a) is ultimately formed; on this basis, the nitrene mechanism previously suggested by Sayo *et al.*^{2e} to explain the formation of the phenazines (3a) and (3b) from the oxidation with lead dioxide of the sulphenanilides (1a) and (1b) was ruled out. We also showed that the chemical behaviour of the radicals (2c) is not dissimilar to that of radicals (2a); thus the absence of (3a) in the oxidation of the sulphenanilide (1c) is not ascribable to further oxidation of the initially formed radicals (2c), as had been previously claimed,^{2e} but to the fact that the reaction leads to the diamine (12c), the final product resulting from O-C-N dimerization of these radicals.

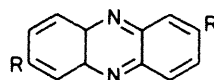
We report here an investigation of the effect of substituents on the reactivity of the thioaminyl radicals (2); this was carried out with 4'-substituted- and 4'-substituted-2-nitro-benzenesulphenanilidyl radicals (2d-j), which were generated by oxidation with lead dioxide of the corresponding anilides (1d-j). The reactions were generally performed both in benzene and acetonitrile (and, in two cases, also in acetone) in



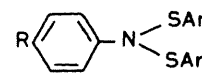
(1)



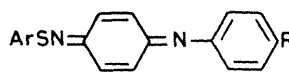
(2)



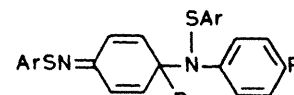
(3)



(4)



(5)



(6)

a; Ar = Ph, R = OMe

b; Ar = Ph, R = Me

c; Ar = C₆H₄NO₂-*o*, R = OMe

d; Ar = Ph, R = H

e; Ar = Ph, R = Cl

f; Ar = Ph, R = Br

g; Ar = Ph, R = NO₂

h; Ar = Ph, R = CN

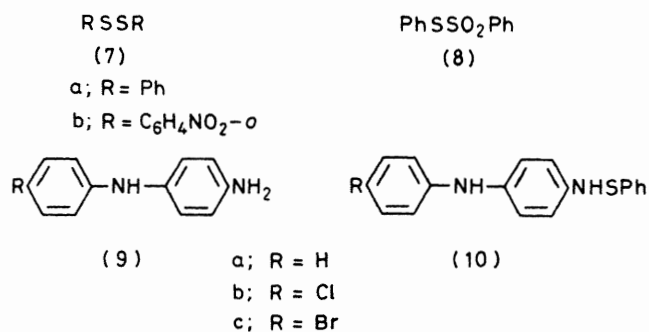
i; Ar = C₆H₄NO₂-*o*, R = Cl

j; Ar = C₆H₄NO₂-*o*, R = NO₂

order to ascertain the extent to which the trend exhibited by the radicals (2) was influenced by varying the solvent polarity. The oxidation of the benzenesulphenanilides (1d), (1e), and (1f) with lead dioxide both in benzene and acetonitrile has been reported^{2e} to lead to the benzenesulphenanilidyl radicals (2d), (2e), and (2f); however the reaction products have not been identified, although it was claimed that the phenazines (3d), (3e), and (3f) are not formed in these reactions on the basis of a spectral investigation.

Results and Discussion

Treatment of a benzene solution of compound (1d) with lead dioxide led to the formation of diphenyl disulphide (7a)



(10%), *N,N*-bis(phenylthio)aniline (4d) (8%), and *N*-phenyl-*N'*-phenylthio-*p*-benzoquinone di-imine (5d) (40%) together with an unknown dark brown product (A); these were the only products isolable by column chromatography. No evidence of phenazine (3d) (nor of any phenazine precursor) could be obtained.

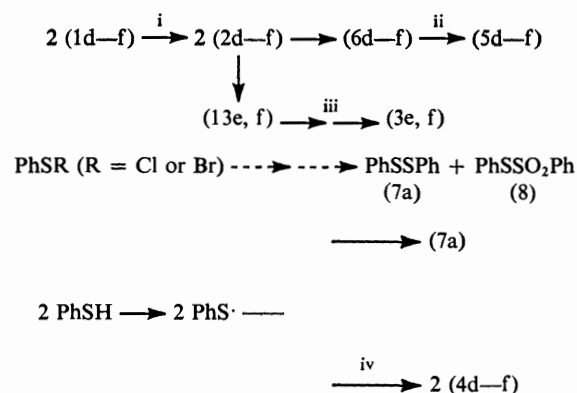
Structural evidence for the *p*-quinone di-imine (5d) was obtained from spectral and chemical data in addition to an elemental analysis. In particular, the mass spectrum showed the molecular ion at *m/z* 290 and predominant ions at *m/z* 181 (*M*⁺ - PhS), 167 (*M*⁺ - PhSN), 155 (*M*⁺ - PhSNC), and 109 (PhS). Chemical proof was obtained by reduction with sodium dithionite which afforded the disulphide (7a) (52%), *N*-phenyl-*p*-phenylenediamine (9a) (29%), and *N*-phenyl-*N'*-phenylthio-*p*-phenylenediamine (10a) (27%).

The di-imine (5d) can be assumed to be formed through *p*-C-N coupling of the radicals (2d) affording the dimeric product (6d), which would then lead to (5d) by loss of thiophenol; under the reaction conditions thiophenol would give phenylthio radicals, which can afford compound (7a) by dimerization and (4a) by coupling with the thioaminy radicals (2d) (Scheme 1).

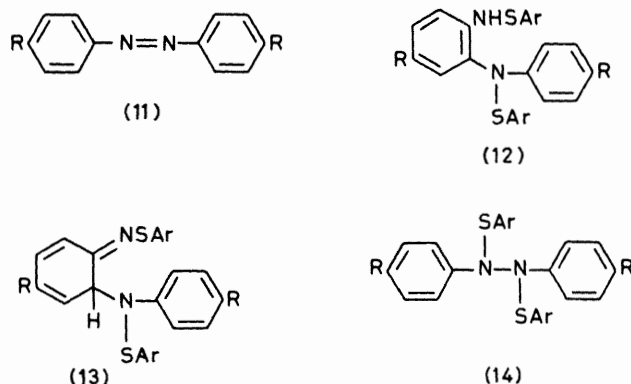
The formation of the di-imine (5d) and the apparent absence of phenazine (3d) (or any precursor), which could be formed by *o*-C-N coupling of the radicals (2d) *via* a pathway analogous to that occurring in the formation of phenazine (3a) from radicals (2a),¹ would indicate that *p*-C-N coupling is largely preferred over *o*-C-N coupling for the parent sulphenanilidyl radicals (2d); an analogous trend has been previously observed with 4-unsubstituted arylaminy radicals.⁴

A similar trend was observed in the oxidation of the sulphenanilides (1e) and (1f) under the same conditions. In fact, these reactions led to the isolation of the disulphide (7a) (22–28%), the anilines (4e) and (4f) (3–9%), and the *p*-quinone di-imines (5e) and (5f) (61–65%) together with small amounts of the phenazines (3e) and (3f). Moreover, phenyl benzenethiosulphonate (8) was isolated in both cases in *ca.* 21% yield. The di-imines (5e) and (5f) were readily identified on the basis of spectral and chemical evidence, by analogy with (5d).

The occurrence of compounds (5e) and (5f) in fairly good yields and of the phenazines (3e) and (3f) in very low yields led to the conclusion that *p*-C-N coupling is also favoured over *o*-C-N coupling for the radicals (2e) and (2f). In fact the di-imines (5e) and (5f) could reasonably arise from *p*-C-N coupling of the radicals (2e) and (2f), leading to the dimers (6e) and (6f) with subsequent loss of PhSR (R = Cl or Br) (Scheme 1). However, at this stage we do not know the way in which the dimers (6e) and (6f) fragment to give (5e) and (5f), and possibly PhSR (R = Cl or Br), and this point was not clarified; therefore, the way in which the disulphide (7a) and the thiosulphonate (8) are produced is not clear at present, although we observed that they result from benzene-sulphenyl chloride under the same reaction conditions.

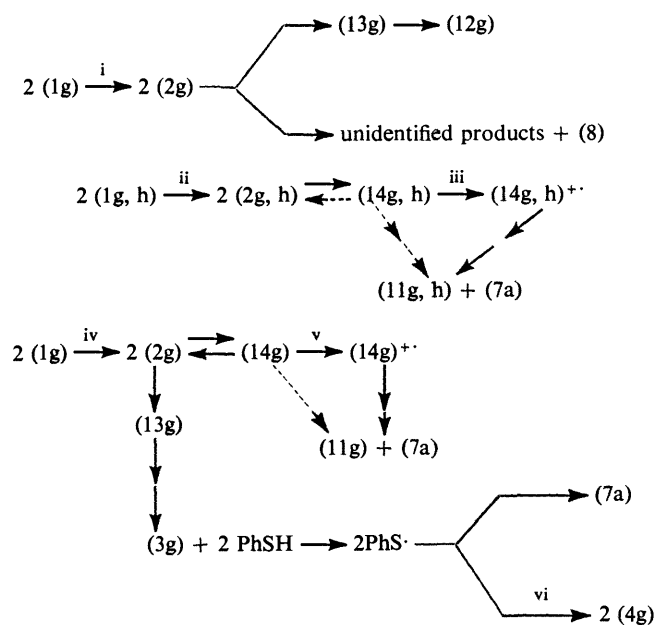


Scheme 1. Reagents: i, PbO₂, benzene; ii, -PhSR (R = H, Cl, or Br); iii, -2 PhSH; iv, 2 (2d-f)



Displacement of halogen has been frequently encountered in reactions of relatively stable halogenated aromatic π radicals;⁵ however, the trend exhibited by radicals (2e) and (2f) is unexpected in the light of previous findings that arylaminy radicals bearing substituents (including halogens) in the *para*-position generally undergo *o*-C-N coupling.^{4,6}

4-Nitrobenzenesulphenanilidyl (2g) was produced by treatment of a benzene solution of (1g) with lead dioxide, which led to a complex reaction mixture from which the disulphide (7a) (5%), the benzenethiosulphonate (8) (33%), the 4,4'-dinitroazobenzene (11g) (2%), and *o*-phenylenediamine (12g) (22%) could be isolated as the only identifiable products together with a number of unknown, highly coloured products. Structural evidence for compound (12g) followed from the i.r. and mass spectral data. The i.r. spectrum showed an NH stretching absorption at 3 390 cm⁻¹. The mass spectrum did not show the molecular ion, but prominent ions at *m/z* 270, 224, 218, 178, 110, and 109 were detected. The ion at *m/z* 270 can be attributed to the 2,7-dinitrophenazine ion, C₁₂H₆N₄O₄⁺, from which the ions at *m/z* 224 (C₁₂H₆N₃O₂⁺), and 178 (C₁₂H₆N₂⁺), are formed as shown by the mass spectrum of pure (3g). The ion at *m/z* 218 is due to the diphenyl disulphide ion, C₁₂H₁₀S₂⁺, from which the ions at *m/z* 110 and 109 arise. Compound (12g) rapidly decomposed in benzene solution at 130 °C, and t.l.c. analysis of the reaction mixture showed the presence of the disulphide (7a) and the phenazine (3g) as the main components together with an unknown yellow product. The diamine (12g) is the product arising from *o*-C-N coupling of radicals (2g) and subsequent isomerization of the resulting dimer (13g); the analogous dimeric product (12c) was isolated from the oxidation of (1c) in benzene¹ (Scheme 2).



Scheme 2. Reagents: i, PbO_2 , benzene; ii, PbO_2 , MeCN, acetone; iii, PbO_2 ; iv, Ag_2O , MeCN; v, Ag_2O ; vi, $2(2g)$

The occurrence of large amounts of unidentified, coloured products accompanying the low yield of *o*-diamine (12g), in addition to the considerable extent of formation of the thio-sulphonate (8), the source of which is unknown, do not allow definite conclusions to be drawn about the chemical behaviour of the radical (2g), although the occurrence of (12g) would be consistent with that expected from 4-substituted arylaminyl radicals.^{4,6}

The apparent trend displayed by radicals (2e—g) was found to change drastically when they were produced in acetonitrile. In fact, whereas we found that oxidation with lead dioxide of the parent benzenesulphenanilide (1d) does not lead to any substantial change when carried out in acetonitrile, as indicated by t.l.c., the disulphide (7a) (ca. 50%) and the phenazines (3e) and (3f) (ca. 65%) were the only identifiable products from the oxidation of (1e) and (1f) in acetonitrile.

On the other hand, oxidation of 4'-nitrobenzenesulphenanilide (1g) afforded (7a) and the azobenzene (11g) in fairly high yields; a similar trend was encountered with 4'-cyano-benzenesulphenanilide (1h) which gave the disulphide (7a) and the 4,4'-dicyanoazobenzene (11h) as the major products, albeit in lower yields. The yields of (11h) and (7a) were found to increase significantly when oxidation of (1h) was carried out in acetone; in this solvent compound (1g) gave the disulphide (7a) and the azobenzene (11g) in almost quantitative yields. Thus it would seem that the thioaminyls (2e) and (2f) resulting from the oxidation of (1e) and (1f) in acetonitrile are trapped as *o*-C-N dimers with eventual formation of the phenazines (3e) and (3f) and the disulphide (7a), whereas the oxidation of (1g) and (1h) in the same solvent and, more effectively, in acetone leads to products which apparently arise from N-N dimerization of the radicals (2g) and (2h) and fragmentation of the resulting N-N dimers (14g) and (14h). In fact, the hydrazines (14g) and (14h) would be reasonable precursors of the azo compounds (11g) and (11h) and the disulphide (7a); this is supported by earlier findings that 3,3',5,5'-tetra-*t*-butylazobenzene is one of the major products from the decomposition of *N,N'*-bis(3,5-di-*t*-butylphenyl)-*N,N'*-bis(4-chlorophenylthio)hydrazine in benzene at room temperature.³

Findings from the oxidation of the benzenesulphenanilides (1d—g) in benzene together with our previous results from the radicals (2a) and (2c) and earlier studies of long-lived thioaminyls indicate that the benzenesulphenanilidyl radicals (2) can undergo N-N dimerization, hydrogen abstraction, and C-N dimerization, in a manner essentially similar to that of arylaminyl radicals.^{4,6} However, since the latter generally undergo *o*-C-N coupling when substituents are present in the *para*-position, the halogen displacement observed with the radicals (2e) and (2f) is noteworthy and, to our knowledge, unprecedented in the chemistry of arylaminyls.

Results obtained from the oxidation of the sulphenanilides (1d—h) in acetonitrile and acetone would appear to indicate that the mode of decomposition of the radicals (2) is noticeably affected by the solvent polarity, at least if 4'-substituents are present; the nature of this effect appears to also be dependent on the nature of the substituent.

If the hydrazines (14g) and (14h) are presumed to be precursors of the azo compounds (11g) and (11h) and the disulphide (7a), results obtained from the oxidation of the benzenesulphenanilides (1g) and (1h) in acetonitrile and acetone might be explained by assuming that, in these solvents, radicals (2g) and (2h) are efficiently trapped as the N-N dimers (14g) and (14h); these can rapidly fragment giving mostly (11g) and (11h) and the disulphide (7a) rather than the original (2g) and (2h) back. On the other hand, N-N dimerization of radicals (2g) and (2h) might be expected to be facilitated owing to stabilization of the resulting N-N dimers (14g) and (14h) by the strong electron-withdrawing substituents in the *N,N'*-phenyl rings, which weaken the dipolar repulsion between the nitrogen atoms and lead to a strengthening of the nitrogen-nitrogen bond.^{2c,7} Moreover, since the azo compound (11g) was found to be formed in very low yield (2%) from the oxidation of (1g) in benzene, formation of the N-N dimer (14g) and/or its fragmentation to (11g) and (7a) should be assumed to be largely disfavoured in this solvent. In our opinion, these results are not satisfactorily explained on the basis of a possible large solvent effect alone and we believe that the oxidant present in the reaction medium is also likely to play some role, possibly determining, in the formation of (11g), (11h) and (7a).

Lead dioxide might be expected to act more rapidly and effectively in polar solvents such as acetonitrile and acetone than in benzene; it is therefore possible that, in acetonitrile and acetone, lead dioxide is capable of oxidising (14g) and (14h) very effectively to the corresponding radical cations (14g, h)^{·+}, thus rapidly removing the hydrazines (14g) and (14h) from their equilibrium with the radicals (2g) and (2h). These radical cations (14g, h)^{·+} would then afford the azo compounds (11g) and (11h) [and the disulphide (7a)], possibly via a mechanism analogous to that occurring in the oxidation of hydrazobenzene derivatives to azobenzenes⁸ (Scheme 2). In fact the radical cations (14g, h)^{·+} might dissociate into sulphenylium ions and hydrazyl radicals,⁹ from which azo compounds (11g) and (11h) would be formed by loss of phenylthio radicals; on the other hand, the unstable sulphenylium ions might be reduced to phenylthio radicals by some species present in the reaction medium.⁹

Support for the intervention of lead dioxide in the formation of the azobenzenes (11g) and (11h) from (14g) and (14h) comes from our results from the oxidation of (1g) with silver(i) oxide in acetonitrile, which gave the azo compound (11g) (13%) and the phenazine (3g) (19%) in addition to *p*-nitro-*N,N*-bis(phenylthio)aniline (4g) (40%) and the disulphide (7a) (19%). These findings, as compared with those obtained from the corresponding reaction of (1g) with lead dioxide, would be explained by assuming that silver(i) oxide brings about a markedly less effective oxidation of hydrazine

(14g) to the radical cations $(14g)^{+\cdot}$, thus resulting in a significant decrease both in the yield of (11g) and in the extent of trapping of radicals (2g) as N-N dimers (14g); the radicals (2g) would then be able to undergo *o*-C-N dimerization, ultimately affording the phenazine (3g), and coupling with phenylthio radicals, leading to (4g), much more favourably than N-N dimerization (Scheme 2).

As for the results from the oxidation of (1e) and (1f), the reasons why the phenazines (3e) and (3f) are formed in acetonitrile at the expense of the di-imines (5e) and (5f) which occur in benzene are less clear at present. Although a possible explanation of the trend observed might be that acetonitrile largely favours *o*-C-N coupling of the radicals (2e) and (2f), whereas *p*-C-N coupling is generally preferred in benzene, we would prefer to suggest that the formation of phenazines (3e) and (3f) might be due to the radical cations $(14e, f)^{+\cdot}$ which would be produced in acetonitrile by oxidation of the N-N dimers (14e) and (14f), as suggested for the radical cations $(14g, h)^{+\cdot}$ (Scheme 3).

In contrast with $(14g, h)^{+\cdot}$, radicals $(14e, f)^{+\cdot}$ would undergo *o*-semidine-like rearrangements leading to (12e) and (12f) (or their precursors), from which the phenazines (3e) and (3f) and the disulphide (7a) would be expected to be formed; analogous rearrangements have been encountered with cation radicals of tetra-*p*-substituted phenylhydrazines, which have been shown to afford dihydrophenazines in a number of instances, although the mechanism of these reactions has not as yet been established.^{10,8}

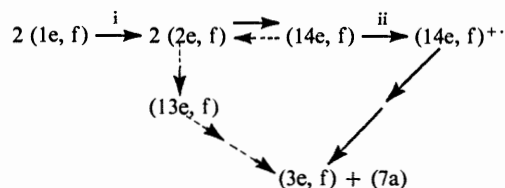
On the other hand, the reasons for the different trend possibly exhibited by cation radicals $(14e, f)^{+\cdot}$ with respect to $(14g, h)^{+\cdot}$ might be ascribed to the effects of the substituents present in the *N,N'*-phenyl rings of $(14)^{+\cdot}$; in fact dissociation of the radical cations $(14)^{+\cdot}$ into aminyl cations and radicals, which might be responsible for the formation of the phenazines (3e) and (3f) from $(14e, f)^{+\cdot}$, would be expected to be less favoured in $(14g, h)^{+\cdot}$ owing to the strong electron-withdrawing nitro and cyano substituents, which should strongly discourage the generation of aminyl cations.

In the light of the results from the oxidation of (1g) with silver(I) oxide, we hoped to find support for the suggested intermediacy of the cation radicals $(14e, f)^{+\cdot}$ in the formation of the phenazines (3e) and (3f) by studying the reaction of (1g) with silver(I) oxide. However, inconclusive evidence was obtained since the reaction both in benzene and acetonitrile led to results not significantly different from those obtained from the corresponding reactions with lead dioxide.

As far as the oxidation of the benzenesulphenanilide (1d) is concerned, results indicate that the chemical behaviour of the parent sulphenanilidyl radicals (2d) is essentially unchanged on passing from benzene to acetonitrile, thus showing that the reactivity of (2d) is virtually unaffected by the solvent polarity.

Finally, the oxidation with lead dioxide of 4'-chloro- and 4'-nitro-2-nitrobenzenesulphenanilides (1i) and (1j) gave results comparable to those obtained with 4'-chlorobenzenesulphenanilide (1e) and 4'-nitrobenzenesulphenanilide (1h), respectively.

In fact the oxidation of (1i) in benzene afforded bis(2-nitrophenyl) disulphide (7b) (11%), the *p*-quinone di-imine (5i) (16%), the diamine (12i) (21%), and traces of the phenazine (3e) as the only identifiable products, whereas the reaction in acetonitrile was shown by t.l.c. to lead to the diamine (12i) as the major product accompanied by minor amounts of an unidentified dark compound; no evidence of the di-imine (5i) could be obtained in this case. Compound (5i) is the di-imine analogue of (5e) isolated from the oxidation of (1e) in benzene, and the diamine (12i) is the dimeric product, the possible precursor of phenazine (3e), analogous to



Scheme 3. Reagents: i, PbO₂, MeCN; ii, PbO₂

the diamine (12c) obtained from the oxidation of (1c). On the other hand, the reaction of 2-nitrobenzenesulphenanilide (1j) in acetonitrile furnished 4,4'-dinitroazobenzene (11g) and bis(2-nitrophenyl) disulphide (7b) in high yields, consistent with the results with sulphenanilide (1g). From these findings, in addition to those previously obtained from the oxidation of (1a) and (1c), it may be inferred that 2-nitrobenzenesulphenanilides on oxidation with lead dioxide also lead to products ascribable to intermediate sulphenanilidyl radicals, thus showing that the trend exhibited by sulphenanilides is independent of the 2-nitro substituent; these results, while supporting our previous evidence which contradicted the claim of Sayo *et al.*,^{2e} would also suggest that the chemical reactivity of benzenesulphenanilidyls is not greatly affected by the presence of the 2-nitro group.

On the basis of all our findings from the study of the reactivity of 4'-substituted- and 4'-substituted-2-nitro-benzenesulphenanilidyl radicals (2a-j) produced by oxidation with lead dioxide from the corresponding benzenesulphenanilides (1a-j) it would appear that the chemical behaviour of these radicals largely depends both on the nature of the 4'-substituent and on the solvent employed, at least under the reaction conditions investigated. However, our present results do not allow any definite conclusions to be drawn as to the probable effects of the lead dioxide on the chemical trends observed, and further studies are in progress to clarify this point.

Experimental

The benzenesulphenanilides (1d-g),^{2a} and the 2-nitrobenzenesulphenanilides (1i) and (1j)^{11,12} were prepared by treating sulphenyl chloride and 2-nitrosulphenyl chloride, respectively, with the corresponding anilines according to known procedures. 4'-Cyanobenzenesulphenanilide (1h) was similarly prepared in *ca.* 40% yield from sulphenyl chloride and 4-cyanoaniline and had m.p. 105–106 °C; ν_{\max} (CS₂) 3340 cm⁻¹; m/z 226 (*M*⁺) and 109. Reaction products, such as diphenyl disulphide (7a),¹³ bis(2-nitrophenyl) disulphide (7b),¹⁴ phenyl benzenethiosulphonate (8),¹⁵ 2,7-dichlorophenazine (3e),¹⁶ 2,7-dibromophenazine (3f),¹² 4,4'-dinitroazobenzene (11g),¹⁷ and 4,4'-dicyanoazobenzene (11h),¹⁸ were each identified by spectral comparison with authentic specimens. Yields of identified products from the oxidation of the benzenesulphenanilides (1d-j) with lead dioxide and silver(I) oxide are given in the Table.

Light petroleum refers to the fraction boiling at 40–60 °C. Column chromatography was carried out on Merck silica gel (0.040–0.063 particle size) or Merck aluminium oxide 90 (0.063–0.200 particle size). Ether refers to diethyl ether.

Oxidation of Benzenesulphenanilides (1d-j). General Procedure.—To a solution of the benzenesulphenanilide (1d-j) (5 mmol) in the appropriate solvent, lead dioxide (*ca.* 25 g) or silver(I) oxide (*ca.* 10 g) was added and the resulting mixtures were vigorously stirred at room temperature, generally

Table. Yields (%)^a of products obtained from the oxidation of benzenesulphenanilides (1d—j)

Benzene-sulphenanilide	Conditions ^b	Product						
		(3)	(4)	(5)	(7)	(8)	(11)	(12)
(1d)	A		8	40	10			
(1e)	A	1	9	65	22	22		
	B	64			44			
(1f)	A	5	3	61	28	21		
	B	63			51			
	C	2	1.5	90	17			
	D	61		5	40			
(1g)	A				5	33		22
	B				73		73	
	D	19	40		19		13	
	E				91		90	
(1h)	B				46		39	
	E				62		78	
(1i)	A	Traces		16	11			21
(1j)	B				82		83	

^a Yields based on 2 mol of (1) giving 1 mol of each of the products. ^b Oxidation carried out with: A, lead dioxide in benzene solution; B, lead dioxide in acetonitrile solution; C, silver(I) oxide in benzene solution; D, silver(I) oxide in acetonitrile solution; E, lead dioxide in acetone solution.

until t.l.c. showed complete disappearance of starting material (24–48 h). The reaction mixture was filtered and the filtrate, after elimination of the excess of solvent, was chromatographed on a silica gel column unless stated otherwise.

Oxidation of Benzenesulphenanilide (1d) with Lead Dioxide in Benzene.—Chromatography on an aluminium oxide column with light petroleum gave (i) the disulphide (7a) and (ii) *N,N*-bis(phenylthio)aniline (4d), m.p. 77–79 °C; v_{\max} (CS₂) 1 210, 750, 738, and 690 cm⁻¹; m/z 309 (*M*⁺), 218, 200, and 109 (Found: C, 69.4; H, 4.95; N, 4.5; S, 21.3. C₁₈H₁₅NS₂ requires C, 69.85; H, 4.9; N, 4.55; S, 20.7%). Elution with 5% ether–light petroleum furnished (i) unchanged (1d) (13%); (ii) *N*-phenyl-*N'*-phenylthio-*p*-benzoquinone di-imine (5d), m.p. 100–102 °C; v_{\max} (CS₂) 1 215, 1 025, 845, 740, and 695 cm⁻¹; m/z 290 (*M*⁺), 181, 167, 155, 109, and 77 (Found: C, 74.15; H, 4.8; N, 9.75; S, 11.15. C₁₈H₁₄N₂S requires C, 74.45; H, 4.85; N, 9.65; S, 11.05%); and (iii) an unidentified dark-violet product (A) (150 mg), m.p. 160–162 °C; v_{\max} (CS₂) 840, 740, and 690 cm⁻¹; m/z 400, 398, 381, 273, 218, 183, and 154 (Found: C, 72.65; H, 4.85; N, 8.45; S, 13.05. Calc. for C₃₀H₂₄N₃S₂: C, 73.45; H, 4.9; N, 8.55; S, 13.05%).

Oxidation of 4'-Chlorobenzenesulphenanilide (1e) with Lead Dioxide.—(a) *In benzene.* Elution with light petroleum gave (i) the disulphide (7a) and (ii) *p*-chloro-*N,N*-bis(phenylthio)aniline (4e), m.p. 78–80 °C; v_{\max} (CS₂) 1 218, 1 210, 820, 740, and 690 cm⁻¹; m/z 343 (*M*⁺), 234, 218, 111, and 109 (Found: C, 62.4; H, 4.05; Cl, 10.45; N, 4.0; S, 18.55. C₁₈H₁₄ClNS₂ requires C, 62.85; H, 4.1; Cl, 10.3; N, 4.05; S, 18.65%). Elution with 5% ether–light petroleum afforded (i) a mixture of three unidentified products (70 mg); (ii) *N*-(*p*-chlorophenyl)-*N'*-phenylthio-*p*-benzoquinone di-imine (5e), m.p. 148–150 °C; v_{\max} (CS₂) 840, 740, 715, 705, and 685 cm⁻¹; m/z 324 (*M*⁺), 218, 215, 186, 111, and 109 (Found: C, 67.0; H, 4.0; Cl, 10.75; N, 8.7; S, 9.95. C₁₈H₁₃ClN₂S requires C, 66.55; H, 4.05; Cl, 10.9; N, 8.65; S, 9.85%); (iii) 2,7-dichlorophenazine (3e); and (iv) phenyl benzenethiosulphonate (8).

(b) *In acetonitrile.* Elution with light petroleum gave compound (7a); elution with 5% ether–light petroleum afforded the phenazine (3e).

Oxidation of 4'-Bromobenzenesulphenanilide (1f).—(a) *With lead dioxide in benzene.* Elution with light petroleum gave

compound (7a) and *p*-bromo-*N,N*-bis(phenylthio)aniline (4f), m.p. 99–101 °C; v_{\max} (CS₂) 1 220, 1 210, 818, 740, and 690 cm⁻¹; m/z 389 and 387 (*M*⁺), 280, 278, 218, 157, and 155 (Found: C, 55.9; H, 3.6; Br, 20.45; N, 3.65; S, 16.3. C₁₈H₁₄BrNS₂ requires C, 55.65; H, 3.65; Br, 20.6; N, 3.6; S, 16.5%). Elution with 5% ether–light petroleum gave (i) *N*-(*p*-bromophenyl)-*N'*-phenylthio-*p*-benzoquinone di-imine (5f), m.p. 145–146 °C; v_{\max} (CS₂) 840, 750, 740, 720, 705, and 690 cm⁻¹; m/z 370 and 368 (*M*⁺), 235, 233, 157, 155, 110, and 109 (Found: C, 58.7; H, 3.4; Br, 21.75; N, 7.7; S, 8.65. C₁₈H₁₃BrN₂S requires C, 58.55; H, 3.5; Br, 21.65; N, 7.6; S, 8.7%); (ii) 2,7-dibromophenazine (3f); and (iii) phenyl benzenethiosulphonate (8).

(b) *With lead dioxide in acetonitrile.* Chromatography gave the disulphide (7a) and the phenazine (3f).

(c) *With silver(I) oxide in benzene.* Chromatography gave (i) the disulphide (7a); (ii) the *p*-bromoaniline (4f); (iii) the di-imine (5f); and (iv) the phenazine (3f).

(d) *With silver(I) oxide in acetonitrile.* Chromatography with light petroleum furnished the disulphide (7a) (27%). Elution with 5% ether–light petroleum gave (i) a mixture of two unidentified, brown products (690 mg), which on heating in boiling acetonitrile were shown by t.l.c. to be rapidly converted into the disulphide (7a) and the phenazine (3f); (ii) the di-imine (5f) (5%); and (iii) the phenazine (3f) (25%). In a repeat experiment, the reaction mixture was refluxed for 5 min and then chromatographed to give (i) the disulphide (7a) (40%); (ii) a mixture of unidentified coloured products (100 mg); (iii) the di-imine (5f) (5%); and (iv) the phenazine (3f) (61%).

Oxidation of 4'-Nitrobenzenesulphenanilide (1g).—(a) *With lead dioxide in benzene.* Elution with light petroleum gave the disulphide (7a); elution with 5% ether–light petroleum afforded 4,4'-dinitroazobenzene (11g) and then phenyl benzenethiosulphonate (8); elution with 15% ether–light petroleum furnished unchanged (1g) (15%) while elution with 25% ether–light petroleum gave 4-nitro-*N*²-(4-nitrophenyl)-*N*¹,*N*²-bis(phenylthio)-*o*-phenylenediamine (12g), m.p. 69–72 °C; v_{\max} (CS₂) 3 390, 1 340, 1 290, 1 115, 755, 740, and 695 cm⁻¹; m/z 270, 224, 218, 178, 110, and 109 (Found: C, 58.2; H, 3.75; N, 11.55; S, 12.9. C₂₄H₁₈N₄O₄S₂ requires C, 58.75; H, 3.7; N, 14.4; S, 13.05%). A solution of compound (12g) (30 mg) in benzene (5 ml) was heated at 130 °C for 2 h, after which time t.l.c. (SiO₂) showed absence of the starting material

(12g) and formation of the disulphide (7a), 2,7-dinitrophenazine (3g), and an unknown yellow compound as the main products. Elution with ether furnished a mixture of unknown, highly coloured products (470 mg).

(b) *With lead dioxide in acetonitrile.* Chromatography afforded the disulphide (7a) and 4,4'-dinitroazobenzene (11g).

(c) *With lead dioxide in acetone.* Chromatography separated compounds (7a) and (11g).

(d) *With silver(i) oxide in acetonitrile.* Elution with light petroleum gave compound (7a), while elution with 5% ether-light petroleum separated (i) *p*-nitro-*N,N*-bis(phenylthio)aniline (4g), m.p. 75–77 °C; v_{\max} (CS₂) 1 340, 1 225, 890, 845, 755, 740, and 690 cm⁻¹; m/z 354 (*M*⁺), 246, 245, 218, and 109; δ (CS₂) 7.13 (10 H, s), 7.58 (2 H, d, *J* 8.5 Hz), and 7.95 (2 H, d, *J* 8.5 Hz) (Found: C, 60.55; H, 4.05; N, 7.8; S, 18.05. C₁₈H₁₄N₂O₂S₂ requires C, 61.0; H, 4.0; N, 7.9; S, 18.1%); and (ii) 4,4'-dinitroazobenzene (11g). Elution with 20% ether-light petroleum gave 2,7-dinitrophenazine (3g), m.p. ca. 270 °C (decomp.) (lit.,¹² 231–234 °C); v_{\max} (CHCl₃) 1 350 cm⁻¹; m/z 270 (*M*⁺), 224, 212, and 178. Elution with ether gave a mixture of unknown products (80 mg).

Oxidation of 4'-Cyanobenzenesulphenanilide (1h) with Lead Dioxide.—(a) *In acetonitrile.* Chromatography with light petroleum gave compound (7a); 10% ether-light petroleum eluted 4,4'-dicyanoazobenzene (11h), while ether eluted intractable material.

(b) *In acetone.* Chromatography separated compounds (7a) and (11h).

Oxidation of 4'-Chloro-2-nitrobenzenesulphenanilide (1i) with Lead Dioxide in Benzene.—Elution with 5% ether-light petroleum gave a mixture of unidentified products (60 mg), and then 2,7-dichlorophenazine (3e); elution with 20% ether-light petroleum gave 4-chloro-*N*²-(4-chlorophenyl)-*N*¹,*N*²-bis(2-nitrophenylthio)-*o*-phenylenediamine (12i), m.p. 205–206 °C; v_{\max} (CHCl₃) 3 400, 1 600, 1 490, 1 480, and 1 345 cm⁻¹; m/z 308, 248, 213, 154, 138, 108, and 106 (Found: C, 51.7; H, 2.85; Cl, 12.55; N, 10.1; S, 11.5. C₂₄H₁₆Cl₂N₄O₄S₂ requires C, 51.5; H, 2.9; Cl, 12.65; N, 10.0; S, 11.45%). A stirred solution of compound (12i) (50 mg) in acetonitrile (50 ml), which contained 1% trifluoroacetic acid, was treated with lead dioxide (200 mg) at room temperature¹ for ca. 15 min. After this time t.l.c. (SiO₂) showed complete disappearance of (12i), 2,7-dichlorophenazine (3e), bis(2-nitrophenyl) disulphide (7b), and *N*-(2-nitrophenylthio)acetamide¹ being the only detectable products.

Continued elution with 20% ether-light petroleum furnished the disulphide (7b), and *N*-(*p*-chlorophenyl)-*N'*-(2-nitrophenylthio)-*p*-benzoquinone di-imine (5i), m.p. 155–157 °C; v_{\max} (CS₂) 1 340, 1 310, 840, 735, and 708 cm⁻¹; m/z 369 (*M*⁺), 242, 241, 154, and 111 (Found: C, 58.6; H, 3.2; Cl, 9.7; N, 11.25; S, 8.6. C₁₈H₁₂ClN₃O₂S requires C, 58.45; H, 3.25; Cl, 9.6; N, 11.35; S, 8.65%). Elution with ether gave a mixture of unidentifiable products (500 mg).

Oxidation of 2,4'-Dinitrobenzenesulphenanilide (1j) with Lead Dioxide in Acetonitrile.—Chromatography with 10% ether-light petroleum afforded 4,4'-dinitroazobenzene (11g); further elution with 20% ether-light petroleum furnished the disulphide (7b).

Reduction of the p-Benzoquinone Di-imine (5d).—A solution of the di-imine (5d) (87 mg) in ether (40 ml) was vigorously shaken with a 20% aqueous solution of sodium dithionite at room temperature for 2 h. The organic layer was separated and the aqueous layer was basified with solid potassium

carbonate and then extracted with ether. The combined ether layers were dried (Na₂SO₄) and concentrated. The residue was chromatographed on an aluminium oxide column, using light petroleum with increasing amounts of ether (up to 50%) as eluant. It was separated, in order of elution, into (i) the disulphide (7a) (13 mg, 52%); (ii) unchanged (5d) (23 mg, 26%); (iii) *N*-phenyl-*N'*-phenylthio-*p*-phenylenediamine (10a) (17 mg, 27%), as a thick oil; v_{\max} (CS₂) 3 420 and 3 390 cm⁻¹; m/z 292 (*M*⁺), 290, 183, 110, and 109 (Found: C, 73.45; H, 5.35. C₁₈H₁₆N₂S requires C, 73.95; H, 5.5%); and (iv) *N*-phenyl-*p*-phenylenediamine (9a) (12 mg, 29%), identical in all respects with an authentic commercial sample.

Reduction of the p-Benzoquinone Di-imine (5e).—This was accomplished by the same procedure as described above for (5d). Chromatography on a silica gel column separated (i) the disulphide (7a) (32%); (ii) unchanged (5e) (10%); and (iii) *N*-(4-chlorophenyl)-*p*-phenylenediamine (9b) (35%), m.p. 69–71 °C (lit.,¹⁹ 70–71 °C).

Reduction of the p-Benzoquinone Di-imine (5f).—To a solution of compound (5f) (100 mg) in dry tetrahydrofuran (100 ml) was added sodium borohydride (400 mg) and the resulting mixture was stirred at room temperature for 12 h. After this time the reaction mixture was poured into water and extracted with ether. The ether layer was separated, washed with water and dried (Na₂SO₄); the excess of solvent was evaporated off and the residue was chromatographed on a silica gel column. Elution with 10% ether-light petroleum separated an unknown product (17 mg) and unchanged (5f) (20 mg, 20%). Elution with 40% ether-light petroleum furnished *N*-(*p*-bromophenyl)-*N'*-phenylthio-*p*-phenylenediamine (10c) (40 mg, 50%), m.p. 108–110 °C; v_{\max} (CS₂) 3 420 and 3 400 cm⁻¹; m/z 372 and 370 (*M*⁺), 264, 263, 262, 261, 218, 110, and 109 (Found: C, 58.45; H, 4.1. C₁₈H₁₅BrN₂S requires C, 58.2; H, 4.05%).

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