Benzenesulphenanilidyl Radicals. Reactivity of 4'-Methoxy- and 4'-Methoxy-2-nitro-benzenesulphenanilidyl Radicals

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Oxidation of 4'-methoxybenzenesulphenanilide (1a) with lead dioxide at 30 °C afforded the *NN*-bis(phenylthio)-*p*-anisidine (7a) and 2,7-dimethoxyphenazine (3a) together with minor amounts of diphenyl disulphide (4a), whereas at 10 °C almost exclusive formation of compound (7a) and the *o*-benzoquinone di-imine (8a) was observed; compound (8a) was found to be thermally unstable and to give, quantitatively, compounds (4a) and (3a). The reaction products are rationalized by assuming that 4'-methoxybenzenesulphenanilidyl radicals (2a), produced by oxidation of compound (1a), undergo C_{ortho}–N coupling to give the dimer (9a), which is responsible for the reaction products observed. A comparable trend was observed by producing the radical (2a) from reaction of compound (1a) with t-butoxy-radicals and by thermal decomposition of compound (7a). These findings rule out the nitrene mechanism previously suggested for the formation of compound (3) from oxidation of the reagent (1a). Evidence has been found that C_{ortho}–N coupling is the main reaction path, exhibited also by 4'-methoxy-2-nitrobenzenesulphenanilidyl radicals (2c) generated from the corresponding anilide (1c) by reaction with t-butoxy-radicals or oxidation with lead dioxide, which thus rejects a previous claim that the radicals (2) (Ar = Ph and Ar = C$_6$H$_4$NO$_2$-*o*) exhibit different chemical behaviour.
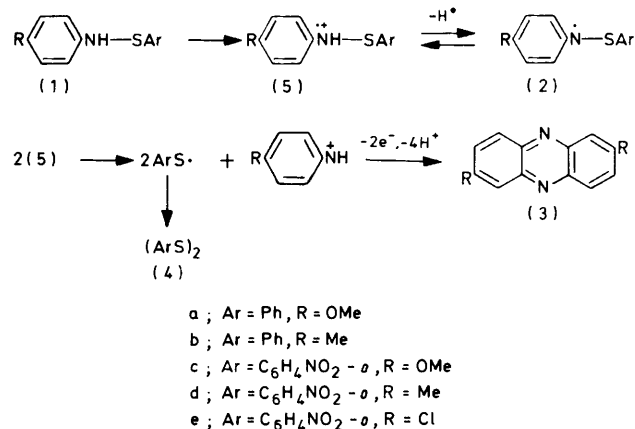
A LARGE number of arylaminyl free radicals, including hydrazyl and N-alkoxyarylaminyl radicals, have been produced and extensive electron spin resonance spectroscopic and chemical investigations have been carried out.[1,2] Recently, a new family of arylaminyl radicals that bear a sulphur atom adjacent to the radical centre, *i.e.* the benzenesulphenanilidyl radicals (2), has been generated and a detailed e.s.r. spectroscopic investigation has been carried out.[3] These radicals have been easily produced from the corresponding benzenesulphenanilides (1) with t-butoxy-radicals or by oxidation with lead dioxide. The e.s.r. data have shown that in the radicals (2) the unpaired electron is distributed mainly around the nitrogen atom and the N-aryl ring, and that the radicals (2), in terms of Walter's criteria, belong to class S.[3a] These radicals are persistent, owing to the significant stabilization by resonance contributions:

$$-\dot{N}-S- \;\longleftrightarrow\; -\bar{N}-\overset{\cdot}{\underset{}{S}}^{+}-$$

Sterically protected thioaminyls are quite persistent and can be isolated as pure crystals [3d] or, at low temperatures, as N–N dimers which dissociate into the radicals (2) at room temperature.[3c] As far as their chemistry is concerned, the only relevant data appear confined to the work of Sayo *et al.*,[4] who carried out an investigation of the oxidation of a number of arenesulphenalides (1) with lead dioxide. It has been reported [4a] that the oxidation of benzenesulphenanilides (1a) and (1b) gives the corresponding 2,7-disubstituted phenazines (3a) and (3b) together with diphenyl disulphide (4a). The reaction products have been accounted for by assuming the formation of benzenesulphenanilidyl radicals (2a) and (2b) (shown by e.s.r. and visible spectra) in protic equilibrium with the radical cations (5a) and (5b); homolytic cleavage of the S–N bond of the radicals (5a) and (5b) has been suggested to afford phenylthio-radicals, which dimerize to the disulphide (4a), and the arenamino-cations (6a) and (6b), from which the phenazines (3a) and (3b) are

believed to be formed by dimerization of intermediate nitrenes, resulting from the cations (6a) and (6b) by a simple proton loss (Scheme 1).

The oxidation of the 2-nitrobenzenesulphenanilides (1c), (1d), and (1e) under the same conditions gave no evidence of formation of the corresponding 2,7-disubstituted phenazines (3).[4a] This difference was explained in terms of a lesser basicity of the nitrogen atom of the cations (5c), (5d) and (5e) with respect to the cations (5a) and (5b), due to the electronegativity of the 2-nitro-group, which causes immediate deprotonation of the cations (5; Ar = C$_6$H$_4$NO$_2$-*o*) to give neutral radicals (2c), (2d), and (2e), from which unidentified products would be formed by further oxidation.

a ; Ar = Ph, R = OMe
b ; Ar = Ph, R = Me
c ; Ar = C$_6$H$_4$NO$_2$ - *o*, R = OMe
d ; Ar = C$_6$H$_4$NO$_2$ - *o*, R = Me
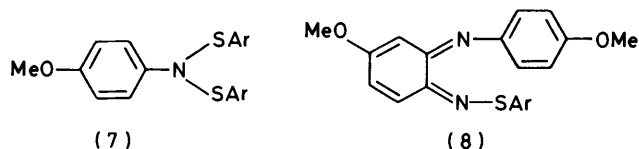e ; Ar = C$_6$H$_4$NO$_2$ - *o*, R = Cl

SCHEME 1

It is known that 4-substituted arylaminyl radicals are usually capable of undergoing C_{ortho}–N coupling followed by isomerization of the resulting dimer to give *o*-phenylenediamines [2b] or, according to the reaction conditions and the nature of the arylaminyl radical, 5,10-dihydrophenazines [1a–c,5] or phenazines [2b,c] which most probably arise from intramolecular cyclization of intermediate phenyl-

enediamines. Thus, formation of the phenazines (3) in the oxidation of 4'-substituted benzenesulphenanilides (1a) and (1b) might be reasonably attributed to an analogous reaction pathway exhibited by the benzene-sulphenanilidyl radicals (2a) and (2b). On this basis, the absence of the phenazines (3) in the oxidation of compounds (1c), (1d), and (1e) might be ascribed to the fact that dimerization of the radicals (2c)—(2e) leads to phenazine precursors that are stable enough to survive under the reaction conditions.

To clarify these points, we undertook a study of the anilidyl radical (2a) and the 2-nitroanilidyl radical (2c), generated by oxidation with lead dioxide of the corresponding anilides (1a) and (1c); the radicals (2) were also generated by hydrogen abstraction from the anilides (1) by t-butoxy-radicals. Treatment of a benzene solution of compound (1a) with lead dioxide at ca. 10 °C for 48 h isolated NN-bis(phenylthio)-p-anisidine (7a) (39%) * and a brown product, which was probably the o-quin-onedi-imine (8a) (54%), together with minor amounts of starting material (13.5%), diphenyl disulphide (4a) (2.7%),* and 2,7-dimethoxyphenazine (3a) (12.5%).*
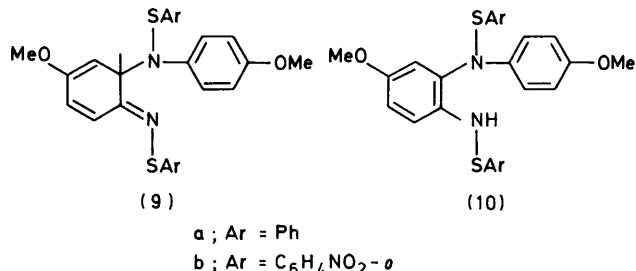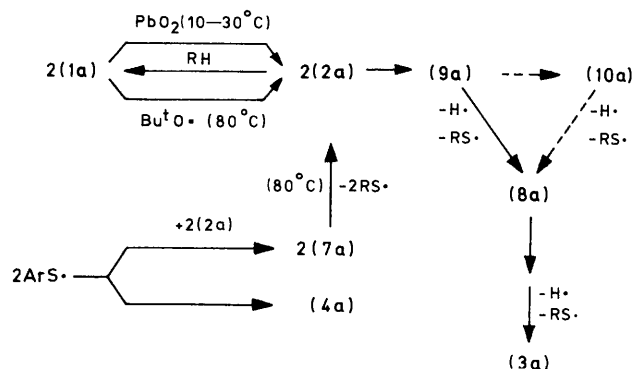

a ; Ar = Ph

b ; Ar = C₆H₄NO₂-o

When the same reaction was carried out at 30 °C, t.l.c. showed that the initial formation of compounds (7a) and (8a) was followed by the slow appearance of compounds (3a) and (4a). After ca. 40 h, the absence of the starting material (1a) and product (8a) was observed. Column chromatography isolated compounds (4a) (8.6%), (7a) (80.4%), and (3a) (34%) as the only identifiable products. Structural evidence for the o-quinonedi-imine (8a) was obtained from spectroscopic and chemical data; elemental analysis was not performed because of the instability of compound (8a). The mass spectrum did not show the molecular ion, and predominant ions at m/z 240, 218, 197, 154, 110, and 109 were observed. The ion at m/z 240 can be assigned to the 2,7-dimethoxyphenazine ion, $C_{14}H_{12}N_2O_2^+$, from which the ions at m/z 197 ($C_{12}H_9N_2O^+$) and 154 ($C_{10}H_6N_2^+$) are formed, as shown by the mass spectrum of pure (3a). The ion at m/z 218 can be attributed to the diphenyl disulphide ion, $C_{12}H_{10}S_2^+$, from which the ions at m/z 110 ($C_6H_6S^+$) and 109 ($C_6H_5S^+$) are produced by fragmentation. The i.r. spectrum exhibited no NH stretching absorption, and the n.m.r. spectrum showed two methoxy-peaks at δ 3.53 and 3.70, in addition to a complex pattern due to 12 protons in the aromatic region. The product (8a) in benzene afforded compounds (3a) and (4a) rather slowly at room tempera-

* Yield is based on 2 mol of starting arenesulphenanilide which will form 1 mol of product.

ture (t.l.c.), while it was rapidly decomposed on refluxing for some minutes to give compounds (3a) (1 mol equiv.) and (4a) (0.5 mol equiv.) in almost quantitative yield. Compound (8a) can reasonably be derived by C_{ortho}-N coupling of the radical (2a) to give the dimer (9a) and then compound (8a) by loss of thiophenol. Isomerization of the dimer (9a) to o-phenylenediamine (10a) and the subsequent loss of thiophenol cannot be ruled out.

(9)   (10)

a ; Ar = Ph

b ; Ar = C₆H₄NO₂-o

This reaction pathway is further supported by our observation that the initial formation of compound (8a) was accompanied by the formation of compound (7a), by coupling of the phenylthio-radical with the fairly persistent radical (2a). Thus, formation of 2,7-dimethoxy-phenazine (3a) in the oxidation of compound (1a) appears to be due to thermal decomposition of the o-quinonedi-imine (8a) to give (3a) and phenylthio-radicals. The reaction scheme for the oxidation of the anilide (1a) is outlined in Scheme 2. Our results are not in agreement

SCHEME 2

with those reported by Sayo et al.[4a] who did not observe any formation of the p-anisidine (7a), which was the major product in our hands; moreover, these authors did not give any evidence of the o-quinonedi-imine (8a), which appears to be the real precursor of the phenazine (3a). This difference may be ascribed to the fact that Sayo et al. separated the phenazine (3a) by repeated extractions of the reaction mixture with 10% hydro-chloric acid; in fact, our control experiments showed that such acid treatment of the reaction mixture completely removes compounds (7a) and (8a), with the disulphide (4a) and phenazine (3a) being the only products detected by t.l.c. Our suggestion that the ben-zenesulphenanilidyl radical (2a) is really involved in the formation of reaction products is supported by results

obtained from reaction of the anilide (1a) with t-butoxy-radicals and from thermal decomposition of the *p*-anisidine (7a). When a benzene solution of compound (1a), which contained an excess of di-t-butyl peroxide, was refluxed for *ca.* 70 h, chromatography of the reaction mixture isolated the products (3a) (33%),* (4a) (26%),* and (7a) (47%) * together with minor amounts of unidentified coloured products. The reaction products can be accounted for by assuming that hydrogen abstraction from compound (1a) by t-butoxy-radicals leads to the radical (2a), from which compounds (3a), (4a), and (7a) arise through the mechanism suggested above. Finally chromatography of the reaction mixture obtained from refluxing for *ca.* 70 h a benzene solution of compound (7a) afforded the products (3a) (50%), (4a) (52%), (1a) (16.7%), and the starting material (7a) (29%). Also, in this case the radical (2a), produced by thermal cleavage of the S–N bond of compound (7a), can be assumed to be the precursor of the reaction products (1a), (3a), and (4a), compound (1a) being the hydrogen abstraction reaction product.
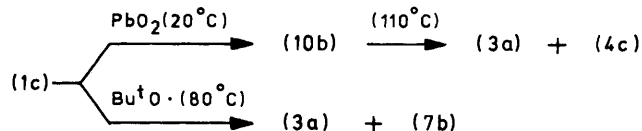
Our findings appear to rule out the mechanism previously suggested for the oxidation of compound (1a), which involves homolytic fragmentation of the radical cation (5a). On this basis, the same conclusion is likely for the mechanism concerning the oxidation of compound (1b).

Oxidation of the anilide (1c) with lead dioxide in benzene at room temperature afforded the diamine (10b) in 75% yield, derived from C_{ortho}–N coupling of the radical (2c) and subsequent isomerization of the dimer (9b), together with starting material (1c) (40%) and minor amounts of an unknown dark brown product. In a repeat experiment, the same reaction led to the complete disappearance of the starting compound (1c), and the yield of the unknown product increased at the expense of compound (10b); moreover, traces of the phenazine (3a) and the disulphide (4c) were also observed. The *o*-phenylenediamine (10b) was identified on the basis of elemental analysis and spectroscopic and chemical evidence. The i.r. spectrum showed NH stretching absorptions at ν 3 400 cm^{-1}. The mass spectrum did not show the molecular ion, but prominent fragment ions were present at *m/z* 396, 308, 240, 197, 155, 154, 138, and 108. The ion at *m/z* 396 arises from the molecular ion by loss of *o*-NO$_2$C$_6$H$_4$S; the ion at *m/z* 308 is assigned to the disulphide ion C$_{12}$H$_8$N$_2$O$_4$S$_2$$^+$ from which ions at *m/z* 155, 154, 138, and 108 are formed, whereas ions at *m/z* 240, 197, and 154 are due to the 2,7-dimethoxy-phenazine ion. The n.m.r. spectrum shows two methoxy-groups at δ 3.7 and 3.78 and a complex multiplet due to 16 protons in the aromatic region. Thermal decomposition of compound (10b) at 110 °C in benzene furnished the disulphide (4c) (14%) and the phenazine (3a) (88%), together with a mixture of unidentified yellow products, possibly arising from further reaction of the 2-nitrophenylthio-radicals, which are known to exhibit a peculiar behaviour because of the *ortho*-nitro-group.[6]

Reaction of compound (1c) with di-t-butyl peroxide
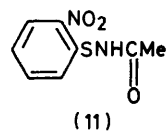
* See footnote on p. 3050.

in refluxing benzene for 70 h gave substantially the same results as obtained from compound (1a). In fact, the phenazine (3a) and the *p*-anisidine (7b) were isolated in 55 and 50% yields,* respectively, with no evidence of compound (10b) (Scheme 3). Formation of the products
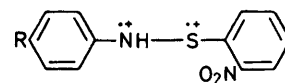

SCHEME 3

(3a) and (7b), together with the absence of (10b), might indicate that under these conditions the dimeric precursor of compound (10b), *i.e.* (9b), undergoes a rapid fragmentation *via* a pathway analogous to that exhibited by compound (9a). Our results show that the radical (2c) behaves analogously to the radical (2a), which is similar to the trend exhibited by *p*-substituted arylaminyl radicals.

The oxidation with lead dioxide of a series of 2-nitrobenzenenesulphenanilides (1c)—(1e) in acetonitrile, which contained 1% trifluoroacetic acid and 1% trifluoroacetic anhydride, has also been investigated by the same authors [4a,b] and shown to lead to diaryl disulphide (4c), phenazines (3), and the acetamide (11). Reaction products have been explained by assuming that in such acid conditions some of the radical cations (5c—e) undergoes homolytic cleavage of S–N bond, but most is further oxidized to the dications (12) without deprotonation. Cleavage of the S–N bond of compounds (12) is claimed to give the cations (6), which would give the phenazines (3), and 2-nitrosulphenylium ion, which would produce compound (11) by electrophilic attack on acetonitrile followed by hydrolysis of the resulting carbonium ion.

Although the effect of the acid on the oxidation of compound (1c) needs to be further investigated, we believe also that in such cases the radicals (2c) might be essentially responsible for the reaction products observed, as possibly supported by our observation that *o*-phenylenediamine (10b) is rapidly destroyed by lead dioxide in acetonitrile solution which contains 1% trifluoroacetic acid and 1% trifluoroacetic anhydride, to give the products (3a) (50%), (4c) (43%), and (11) (31%) together with minor amounts of unidentified yellow products. However, all our attempts to show the intermediacy of compound (10b) in the oxidation of compound (1c) in acid conditions were unsuccessful.

EXPERIMENTAL

4′-Methoxybenzenesulphenanilide (1a) and 4′-methoxy-2-nitrobenzenesulphenanilide (1c) were prepared according to

the literature.[7,8] Reaction products, such as diphenyl disulphide (4a),[9] bis-(2-nitrophenyl) disulphide (4c),[10] and 2,7-dimethoxyphenazine (3a)[11] were always identified by spectral comparison with authentic specimens.

Reaction of 4'-Methoxybenzenesulphenanilide (1a) *with Lead Dioxide.*—(a) *Oxidation of compound* (1a) *at* 10 °C. Lead dioxide (2.70 g) was added in *ca.* 15 min to a solution of compound (1a) (0.55 g, 2.40 mmol) in dry benzene (250 ml), with vigorous stirring, at *ca.* 10 °C The solution became blue and then yellow-green. T.l.c. (Al_2O_3) showed formation of compounds (7a) and (8a) after 1—2 h, whereas compounds (3a) and (4a) were detected only after *ca.* 20 h. The mixture was stirred for 48 h at 10 °C. After this time the reaction mixture was filtered and the filtrate chromatographed on an aluminium oxide column. Elution with light petroleum (b.p. 40—60 °C) afforded (i) diphenyl disulphide (4a) (0.007 g, 0.032 mmol., 2.7%) and (ii) NN-*bis-(phenylthio)-p-anisidine* (7a) (0.16 g, 0.47 mmol, 39% m.p.), 106—108 [°C; $\nu_{max.}$ (CS_2) 1 250, 1 200, 1 040, 820, and 830 cm^{-1}; *m/z* 339 (M^+), 231, 230, 218, 122, and 109; $\delta(CS_2)$ 3.6 (3 H, s) and 6.4—7.3 (14 H, m) (Found: C, 67.45; H, 5.1; N, 4.1; S, 18.75. $C_{19}H_{17}NOS_2$ requires C, 67.2; H, 5.05; N, 4.15, S, 18.9%).

Continued elution with solvent of increasing polarity (up to light petroleum–diethyl ether, 1 : 1) separated a brown solid, which was probably 4-methoxy-N^2-(*p*-methoxyphenyl)-N^1-phenylthio-*o*-benzoquinone di-imine (8a) (0.23 g, 0.65 mmol, 54%); $\nu_{max.}$ 1 635 and 1 245 cm^{-1}; *m/z* 240, 218, 197, 154, 110, and 109; $\delta(CDCl_3)$ 3.53 (3 H, s), 3.70 (3 H, s), and 5.9—7.6 (12 H, m); unchanged (1a) (0.076 g, 0.33 mmol, 13.5%); and 2,7-dimethoxyphenazine (3a) (0.036 g, 0.15 mmol, 12.5%).

(b) *Oxidation of compound* (1a) *at* 30 °C. A solution of compound (1a) (0.96 g, 4.15 mmol) in dry benzene (400 ml) was treated with lead dioxide (4.72 g) at 30 °C as described above. T.l.c. (Al_2O_3) showed initial formation of the products (7a) and (8a) and, after *ca.* 2 h, of compound (3a). After *ca.* 40 h compounds (1a) and (8a) were absent, as monitored by t.l.c. At this time the reaction mixture was filtered and the filtrate was chromatographed on an aluminium oxide column, using light petroleum (b.p. 40—60 °C) which contained an increasing percentage of diethyl ether (up to 50%) as eluant. It was separated, in order of elution, into (i) diphenyl disulphide (4a) (0.039 g, 0.179 mmol, 8.6%); (ii) the *p*-anisidine (8a) (0.566 g, 1.67 mmol, 80.4%); and (iii) 2,7-dimethoxyphenazine (3a) (0.17 g, 0.71 mmol, 34%).

(c) *Acid treatment of the reaction mixture.* A mixture obtained from the oxidation of compound (1a) (0.18 g) with method (a) was filtered and the filtrate was extracted with 10% hydrochloric acid (3 × 40 ml). The benzene layer was assayed by t.l.c. and diphenyl disulphide (4a) was the only product detected. The aqueous solution was basified with ammonium hydrate and extracted with chloroform; t.l.c. of the organic layer showed the presence of 2,7-dimethoxyphenazine (3a) as the only detectable product.

Thermal Decomposition of the o-Benzoquinonedi-imine (8a). —A solution of compound (8a) (0.21 g, 0.60 mmol) in benzene (50 ml) was refluxed for *ca.* 20 min; the solvent was evaporated off and the residue chromatographed on an aluminium oxide column. Elution with pentane gave diphenyl disulphide (4a) (0.054 g, 0.25 mmol, 83%); elution with pentane–diethyl ether (1 : 1) afforded 2,7-dimethoxyphenazine (3a) (0.118 g, 0.49 mmol, 82%).

Reaction of the Anilide (1a) *with Di-t-butyl Peroxide.*—A

solution of compound (1a) (0.46 g, 2.0 mmol) and di-t-butyl peroxide (8 ml) in benzene (160 ml) was refluxed until t.l.c. (Al_2O_3) showed the disappearance of compound (1a) (*ca.* 70 h). The reaction mixture was chromatographed on a silica gel column. Elution with pentane gave diphenyl disulphide (4a) (0.056 g, 0.26 mmol, 26%); elution with pentane–diethyl ether (9 : 1) afforded the *p*-anisidine (7a) (0.16 g, 0.472 mmol, 47%); elution with diethyl ether furnished a mixture of two unidentified orange products (0.045 g) and 2,7-dimethoxyphenazine (3a) (0.08 g, 0.33 mmol, 33%).

Thermal Decomposition of the Anisidine (7a).—A solution of compound (7a) (0.176 g, 0.52 mmol) in benzene (50 ml) was refluxed for *ca.* 70 h. Chromatography of the reaction mixture on a silica gel column afforded (i) diphenyl disulphide (4a) (0.059 g, 0.273 mmol, 52%); (ii) unchanged (7a) (0.052 g, 0.153 mmol, 29%); (iii) the anilide (1a) (0.02 g, 0.087 mmol, 16.7%); and (iv) 2,7-dimethoxyphenazine (3a) (0.031 g, 0.129 mmol, 50%).

Reaction of the Anilide (1c) *with Lead Dioxide.*—(a) *Oxidation of compound* (1c) *in benzene.* To a solution of compound (1c) (1.38 g, 5.0 mmol) in dry benzene (400 ml) was added lead dioxide (5.4 g), and the resulting mixture was stirred at room temperature for 48 h. After this time the reaction mixture was filtered and the filtrate was chromatographed on a silica gel column. Elution with pentane–diethyl ether (4 : 1) afforded the starting material (1c) (0.55 g, 40%); (ii) 4-methoxy-N^2-(4-methoxyphenyl)-N^1N^2-bis-(2-nitrophenylthio)-*o*-phenylenediamine (10b) (0.63 g, 1.15 mmol, 76%) as yellow-orange crystals, m.p. 166—167 °C, $\nu_{max.}$ ($CHCl_3$) 3 400, 2 840, 1 600, and 1 340 cm^{-1}; *m/z* 396, 308, 240, 197, 155, 154, 138, and 108; $\delta(CDCl_3)$ 3.7 (3 H, s), 3.78 (3 H, s), and 6.5—8.45 (16 H, m) (Found: C, 56.45; H, 4.0; N, 10.25; S, 11.75. $C_{26}H_{22}N_4O_6S_2$ requires C, 56.7; H, 4.05; N, 10.2; S, 11.65%); and (iii) an unknown dark-brown product (0.05 g), m.p. 120—122 °C (decomp.). In a a repeated experiment, the same reaction led to complete disappearance of the starting material (1e); chromatography of the reaction mixture afforded compound (10b) (0.68 g, 1.24 mmol, 50%) and the unknown dark brown product (0.32 g), together with traces of 2,7-dimethoxyphenazine (3a) and bis-(2-nitrophenyl) disulphide (4c).

(b) *Oxidation of compound* (1c) *in acetonitrile which contained trifluoroacetic acid.* A stirred solution of compound (1c) (0.14 g) in acetonitrile (40 ml), which contained 1% trifluoroacetic acid and 1% trifluoroacetic anhydride was treated with lead dioxide (0.54 g) at room temperature. The reaction was followed by t.l.c. (SiO_2); no formation of the *o*-phenylenediamine (10b) nor of the unknown dark brown product was observed. The starting material (1c) almost completely disappeared after *ca.* 15 min and 2,7-dimethoxyphenazine (3a), bis-(2-nitrophenyl) disulphide (4c), and *N*-(2-nitrophenylthio)acetamide (11) were the only detectable products.

Reaction of the Anilide (1c) *with Di-t-butyl Peroxide.*—A solution of compound (1c) (0.32 g, 1.16 mmol) and di-t-butyl peroxide (4 ml) in benzene (100 ml) was refluxed until t.l.c. (SiO_2) showed the disappearance of compound (1c) (*ca.* 60 h) and the reaction mixture was chromatographed on a silica gel column. Elution with pentane gave (i) a mixture of unidentified products (0.06 g); (ii) the *p*-anisidine (7b) (0.12 g, 0.28 mmol, 48%) as yellow-orange crystals, m.p. 167—168 °C; $\nu_{max.}$ ($CHCl_3$) 2 840, 1 600, and 1 340 cm^{-1}; *m/z* 429, 308, 275, 154, and 122 (Found: C, 52.95; H, 3.55; N, 9.75; S, 15.05. $C_{19}H_{15}N_3O_5S_2$ requires C, 53.15; H, 3.5; N, 9.8; S, 14.95%). Elution with pentane–diethyl

ether (1 : 1) afforded an unidentified reddish product (0.02 g) and 2,7-dimethoxyphenazine (3a) (0.075 g, 0.31 mmol, 54%).

Thermal Decomposition of the o-*Phenylenediamine* (10b).— A solution of compound (10b) (0.2 g, 0.36 mmol) in benzene (20 ml) was kept at 110 °C for 12 h. Chromatography on a silica gel column of the reaction mixture afforded bis-(2-nitrophenyl) disulphide (4c) (0.016 g, 0.052 mmol, 14%), 2,7-dimethoxyphenazine (3a) (0.078 g, 0.325 mmol, 88%), and a mixture of yellow products (0.04 g).

Oxidation of the o-*Phenylenediamine* (10b) *in Acetonitrile Solution that contains Trifluoroacetic Acid.*—A stirred solution of compound (10b) (0.25 g, 0.455 mmol) in acetonitrile (150 ml) which contained 1% trifluoroacetic acid and 1% trifluoroacetic anhydride was treated with lead dioxide (0.4 g) at room temperature. After the starting material (10b) had disappeared (by t.l.c.; *ca.* 20 min), the mixture was treated with solid potassium carbonate, filtered, and the filtrate chromatographed on a silica gel column. Elution with pentane which contained an increasing percentage of diethyl ether (up to 80%) furnished (i) bis-(2-nitrophenyl) disulphide (4c) (0.06 g, 0.19 mmol, 43%); (ii) 2,7-dimethoxyphenazine (3a) (0.055 g, 0.23 mmol, 50%); (iii) a mixture of unidentified yellow products (0.035 g); and (iv) *N*-(2-nitrophenylthio)acetamide (11) (0.06 g, 0.28 mmol, 31%), m.p. 190—192 °C (decomp.) (lit.,[4a] 179—180 °C), identical in all respects with an authentic specimen independently prepared from 2-nitrobenzenesulphenyl chloride and acetamide.[4a]

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