

Oxidative, Photoinduced, and Thermal Sulphur–Nitrogen Bond Fission in Benzenesulphenanilides

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The reaction of *NN*-bis-*p*-methoxyphenylbenzenesulphenamide (1) in liquid sulphur dioxide afforded bis-*p*-methoxyphenylamine, diphenyl disulphide, *p*-methoxyanilino-5-methoxyphenyl phenyl sulphide, and 5,10-dihydro-2,7-dimethoxy-5,10-bis-*p*-methoxyphenylphenazine through oxidative cleavage of the S–N bond of (1). The reaction of the sulphenamide (1) with aniline in liquid sulphur dioxide gave benzenesulphenanilide, suggesting the formation of benzenesulphenylium ion in this solvent. Rearrangement products were also obtained by thermolysis and photolysis of some sulphenanilides.

TETRAKIS-*p*-METHOXYPHENYLHYDRAZINE (7) and tetra-*p*-tolylhydrazine rearrange in liquid sulphur dioxide to the corresponding dihydrophenazines *via* cation radicals.¹ Furthermore a mixture of the above hydrazines in this solvent affords the phenazine cross-product.² In the light of these results we have examined the reactions of benzenesulphenanilides having low ionization potentials with sulphur dioxide, expecting the occurrence of oxidative S–N bond fission. We hoped that comparison of the results with those of the reactions of the tetra-arylhydrazines would clarify the mechanisms of both reactions. Oxidation of sulphenamides with conventional oxidants (KMnO₄, H₂O₂, or Na₂O₂) affords only the corresponding sulphonamides.³ We were also interested in studying photoinduced and thermal S–N bond fission of sulphenanilides with regard to the

behaviour of the resulting thio- and anilino-radicals. Thermolysis⁴ and photolysis⁵ of 2-nitrobenzenesulphenanilide have been examined previously, giving 2-aminobenzenesulphonanilide, from coupling of an anilino-radical with a 2-aminobenzenesulphonyl radical as a principal product. 2-Aminobenzenesulphonyl radical is considered to be formed from 2-nitrobenzenesulphenyl radical by intramolecular transfer of oxygen from the nitro-group to the sulphur.

RESULTS AND DISCUSSION

The reactions of sulphenanilides in liquid sulphur dioxide were performed at 20 °C in the absence of oxygen. U.v. and e.s.r. spectra of the mixture were measured periodically.

³ H. Fox, P. Diedrich, and M. Dohrn, U.S.P., 2,476,655/1949.

⁴ F. A. Davis and R. P. Johnson, jun., *J. Org. Chem.*, 1972, **37**, 854.

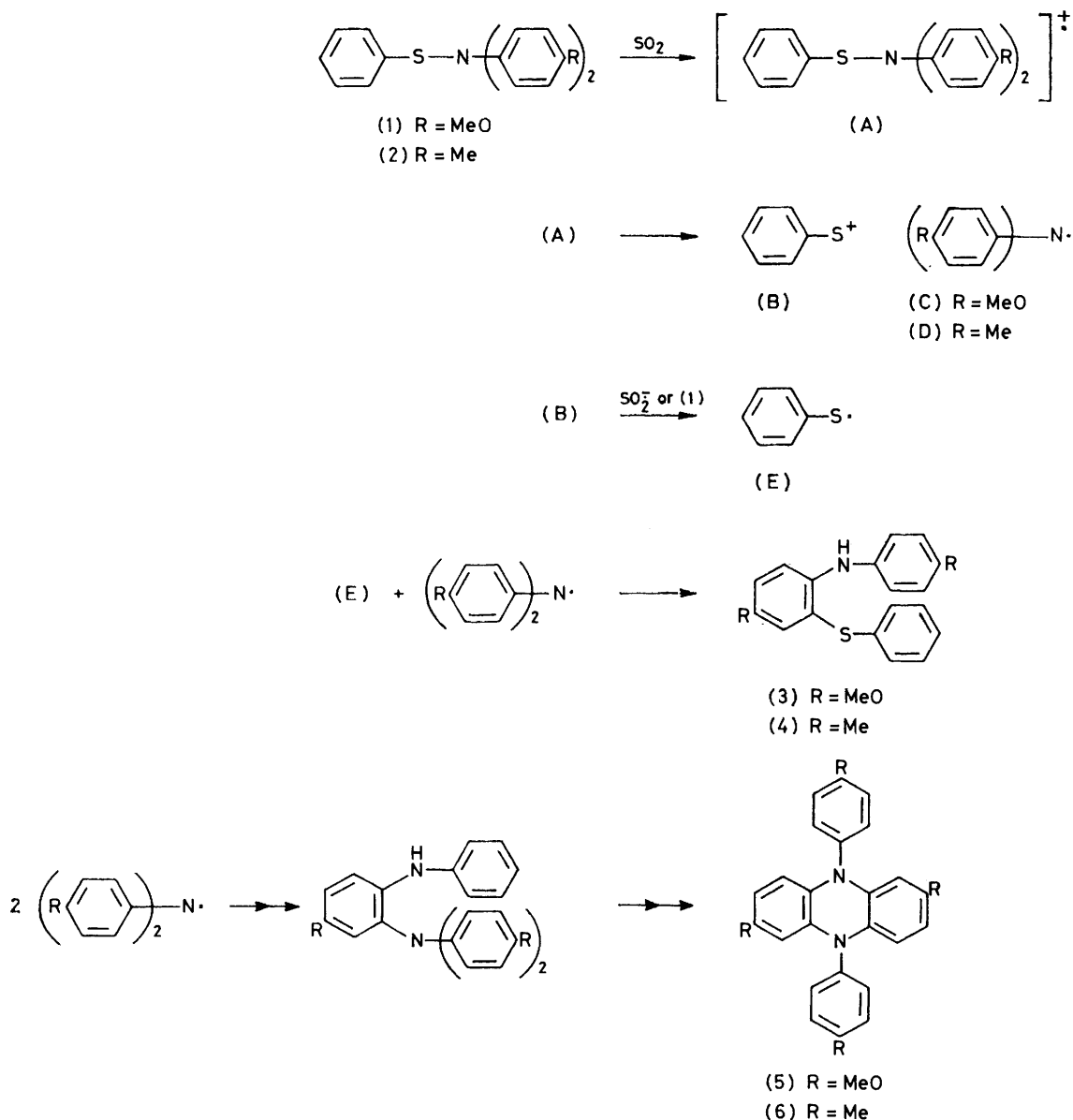
⁵ D. H. R. Barton, T. Nakano, and P. G. Sammes, *J. Chem. Soc. (C)*, 1968, 322.

¹ M. Nojima, T. Ando, and N. Tokura, *J.C.S. Perkin I*, 1976, 1504.

² T. Ando, M. Nojima, and N. Tokura, *J.C.S. Chem. Comm.*, 1975, 989.

When *NN*-bis-*p*-methoxyphenylbenzenesulphenamide (1) was dissolved in liquid sulphur dioxide, the absorption at 665 nm attributable to the cation radical of (1) was observed. After 40 min the absorption started to decay, and new bands attributable to a mixture of bis-*p*-methoxyphenylaminyl radical (C) (λ_{\max} 740 nm)⁶

served in the reaction of *NN*-di-*p*-tolylbenzenesulphenamide (2). The solution in sulphur dioxide showed u.v. absorption assignable to a mixture of di-*p*-tolylaminyl radical (D) (λ_{\max} 730 nm)⁶ and the corresponding dihydrophenazine (6) cation radical (λ_{\max} 450 and 490 nm).¹ E.s.r. spectroscopy only showed the presence of



SCHEME 1

and 5,10-dihydro-2,7-dimethoxy-5,10-bis-*p*-methoxyphenylphenazine (5) (λ_{\max} 490, 535, and 650 nm)¹ appeared and increased in intensity. The e.s.r. spectrum of this solution only showed the presence of the cation radical of (5).¹ From the reaction mixture bis-*p*-methoxyphenylamine (10), diphenyl disulphide (9), 2-(*p*-methoxyanilino)-5-methoxyphenyl phenyl sulphide (3), and the phenazine (5) were obtained in yields of 80, 80, 1, and 1%, respectively. Similar behaviour was ob-

the cation radical of (6).¹ Di-*p*-tolylamine (11), compounds (9) and (6), and 2-(*p*-tolylamino)-5-methylphenyl phenyl sulphide (4) were isolated in yields of 13, 13, 0.2, and 0.2%, respectively [with starting material (71%)].

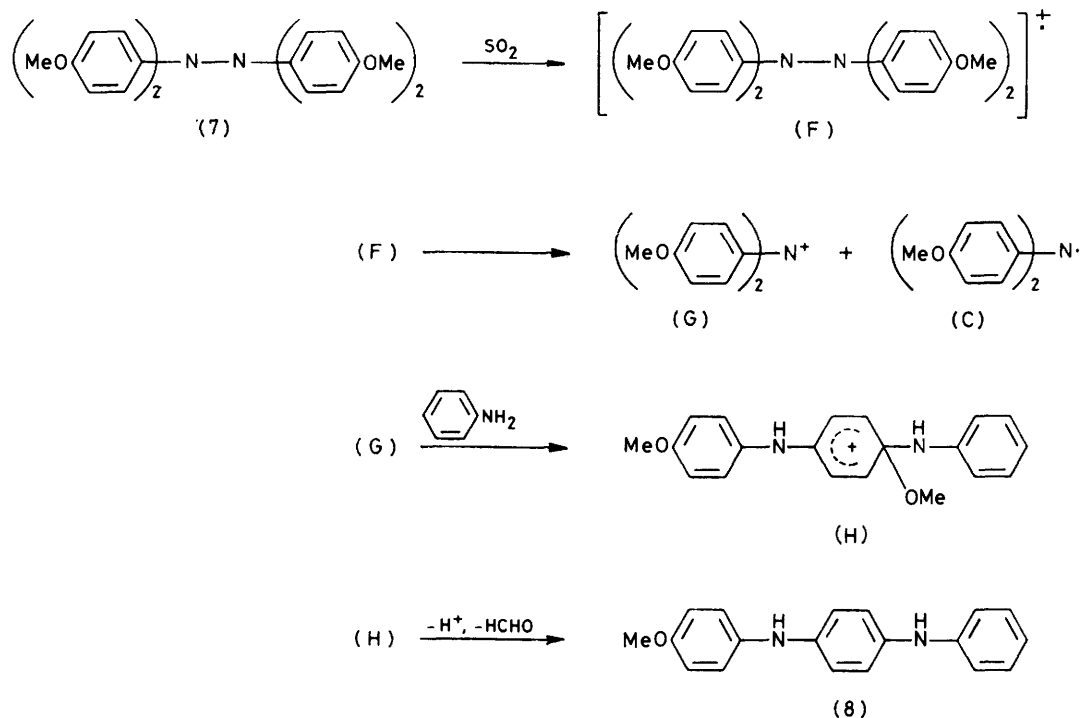
To explain the above results the mechanism shown in Scheme 1 appears the most probable. Electron transfer between (1) and sulphur dioxide may occur in the first

⁶ F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, 1965, **98**, 844.

step, affording the cation radical of (1), which may dissociate into the sulphenylium ion (B) and the aminyl radical (C). The unstable sulphenylium ion⁷ may then be reduced by an ambient anion or by (1) to the thio-radical (E),⁸ which will dimerize to give (9) and also attack (C) at the *ortho*-position to form (3). Exclusive *ortho*-coupling of (C) followed by intramolecular cyclization may afford (5).⁹ The radical (C) can also abstract a hydrogen atom giving (10).

since 71% of the starting material was recovered in the reaction of (2), which is considered to have a higher ionization potential than (1), we prefer to regard the electron transfer between (1) and sulphur dioxide as the first step of the reaction.

To ascertain whether the cation radical (F) of the hydrazine (7) might dissociate to the aminyl cation (G) and (C) in liquid sulphur dioxide, the reaction of (7) with aniline in this solvent was examined. U.v. and



SCHEME 2

To obtain evidence for the formation of the sulphenylium ion (B), the reaction of (1) in sulphur dioxide in the presence of aniline was investigated. After 24 h benzenesulphenanilide (15) was obtained in 46% yield, with a 53% yield of (9) and a 92% yield of (10). To eliminate the possibility that (15) was obtained by attack of aniline on the sulphur atom of (1), the reaction of (1) in ether was also examined; only starting material was recovered. From the reaction of (1) in the absence of aniline, only the products derived from the thio-radical [(3) and (9)] were obtained. This supports the hypothesis that the first-formed ion (B) is reduced in the absence of a nucleophile to a thio-radical, which affords (3) and (9). We cannot discount a different process from that shown in Scheme 1 for the formation of (B): sulphur dioxide, a weak Lewis acid¹⁰ may attack the nitrogen atom of (1), and heterolysis of the S-N bond would then afford probably a mixture of (B), (C), and the radical anion of sulphur dioxide. However

e.s.r. spectra suggested the formation of (F)¹ in the first step, and a weak absorption attributable to the cation radical of (5) was observed later. A 10% yield of *N-p*-methoxyphenyl-*N'*-phenyl-*p*-phenylenediamine (8) was obtained. The formation of (8) may be explained in terms of attack of aniline on (G) at the *para*-position, followed by the elimination of a proton and formaldehyde (Scheme 2). This is consistent with the result that cyanide ion attacks (G) selectively at the *para*-position.¹¹ The elimination of a methoxy-group from an intermediate such as (H) is well known.¹² In the absence of a nucleophile, (G) may be reduced by (7) or an ambient anion to the aminyl radical (C), which affords the corresponding dihydrophenazine and amine.¹

The sulphide (3) may be formed by the coupling of the thio-radical and the aminyl radical. To obtain evidence for this, we examined the photolysis of (1) in *n*-pentane, and obtained (3) in 30% yield, with (9) and

⁷ G. Capozzi, V. Lucchini, G. Modena, and F. Rivetti, *J.C.S. Perkin II*, 1975, 361.

⁸ N. Kharasch and M. M. Wald, *Analyt. Chem.*, 1955, **27**, 996.

⁹ F. A. Neugebauer and H. Fischer, *Chem. Ber.*, 1971, **104**, 886.

¹⁰ N. Kakeya, M. Nojima, and N. Tokura, *J.C.S. Perkin I*, 1976, 87.

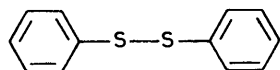
¹¹ D. Serve, *J. Amer. Chem. Soc.*, 1975, **97**, 432.

¹² S. Andreaders and E. W. Zahnow, *J. Amer. Chem. Soc.*, 1969, **91**, 4181.

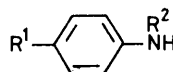
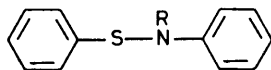
(10). It is well established¹³ that photo-Fries products are obtained by rearrangement of the diradical produced in the solvent cage by homolytic cleavage of a bond between two heteroatoms. On the other hand, a photo-degradation product is obtained from a radical which has escaped from the cage. Irradiation of compounds (2), (14), and (15) also gave mixtures of photo-Fries products (sulphides) and degradation products [anilines

sulphide is formed by the combination of thio- and aminyl radicals. Homolysis of an S-N bond has been proposed for the photolysis of 2-nitrobenzenesulphenanilide.⁵

Thermal reactions of sulphenanilides in *N*-methyl-2-pyrrolidone also afforded rearrangement products and degradation products (Table). The yields of sulphides were lower than in the photolysis in *n*-pentane. This

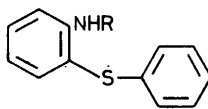


(9)

(10) R¹ = MeO, R² = *p*-MeO·C₆H₄(11) R¹ = Me, R² = *p*-Me·C₆H₄(12) R¹ = H, R² = Me(13) R¹ = H, R² = H

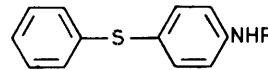
(14) R = Me

(15) R = H



(16) R = Me

(17) R = H



(18) R = Me

(19) R = H

and (9)] (Table). These data indicate that the yield of photo-Fries products increases as the stability of the corresponding aminyl radical increases. Unstable aminyl radicals may escape rapidly from the cage and abstract

hydrogen to give anilines. On the other hand, diarylaminyl radicals are reported not to be very active as hydrogen-abstraction reagents, even in conjunction with such reactive hydrocarbons as cumene, tetralin, and cyclohexene.¹⁴ Although decisive evidence was not obtained for homolytic bond fission of sulphenanilides under these reaction conditions [the e.s.r. spectrum of a solution of (1) and (2) in *n*-pentane exposed to light consists of weak, broad signals], we consider that the

may be due to the ease of hydrogen abstraction by the aminyl radical from *N*-methyl-2-pyrrolidone. By heating compound (1) at 175 °C or (2) at 215 °C strong, broad e.s.r. signals (total width 35 and 36 mT, respectively) were obtained, suggesting the occurrence of homolysis of the S-N bond. Similar behaviour was observed in the thermolysis of *N*-cyclohexylbenzothiazole-2-sulphenamide.¹⁵ The above data support the hypothesis that benzenesulphenyl radical and bis-*p*-methoxyphenylaminyl radical formed from (1) in sulphur dioxide yield the rearrangement product (3) but in low yield, because the radicals are considered not to be formed in the solvent cage.

Photolysis and thermolysis of sulphenanilides

Sulphenanilide	Products [%]
(3) ^a	(3) [30], (10) [14], (9) [14]
(3) ^b	(3) [10], (10) [74], (9) [74]
(8) ^a	(4) [39], (11) [40], (9) [43]
(8) ^b	(4) [9], (11) [65], (9) [65]
(14) ^a	(16) [15], (18) [14], (12) [21], (9) [39]
(14) ^b	(16) [5], (18) [5], (12) [50], (9) [90]
(12) ^{a,c}	(17) [9], (19) [8], (13) [35], (9) [34]
(12) ^b	(13) [53], (9) [97]

^a A solution of sulphenanilide in *n*-pentane was irradiated with a PIH 300 W high-pressure mercury lamp. ^b Reactions at 202 °C. ^c Starting material (19%) recovered.

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¹³ D. Masilami, R. O. Hutchins, and J. Ohr, *J. Org. Chem.*, 1976, **41**, 3687, and references therein.

¹⁴ S. F. Nelsen, 'Free Radicals', vol. 2, ed. J. K. Kochi, Wiley-Interscience, New York, 1973, p. 534.

¹⁵ I. I. Eittington, M. M. Krauskhina, S. N. Kavun, N. P. Srel'nikova, and V. K. Butyugin, *Kauch. Rezina*, 1965, **24**, 9 (*Chem. Abs.*, 1965, **63**, 18,064f).

EXPERIMENTAL

E.s.r. spectra were obtained with a JEOL JNM 4P100 instrument, u.v. spectra with a Varian Techtron 635 spectrometer, ¹H n.m.r. spectra with a JEOL 3H-60 instrument, and mass spectra with a Hitachi RMU-6H spectrometer. The details of the apparatus used for the reactions in liquid sulphur dioxide have been described previously.¹⁶

Tetra-*p*-methoxyphenylhydrazine,⁶ *N*-methylbenzenesulphenanilide,¹⁷ and benzenesulphenanilide¹⁸ were prepared by reported methods.

Synthesis of NN-Bis-p-methoxyphenylbenzenesulphenamide.—To a solution of bis-*p*-methoxyphenylamine (0.01 mol) and triethylamine (0.01 mol) in ether (40 ml) was added benzenesulphenyl chloride (0.01 mol) in ether (50 ml)

¹⁶ T. Nagai, T. Miyazaki, Y. Sonoyama, and N. Tokura, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3087.

¹⁷ J. Kordeeler and B. Redies, *Chem. Ber.*, 1959, **92**, 1.

¹⁸ H. Lecher, F. Holschneider, K. Koberler, W. Speer, and P. Stocklin, *Ber.*, 1925, **58**, 409.

during 15 min at 0 °C. The mixture was warmed to room temperature, and the reaction was continued for a further 1 h. The precipitated salt was filtered off and the filtrate was condensed under reduced pressure. The crude sulphenamide was purified by column chromatography (twice) on basic alumina (elution with light petroleum) to give a liquid (60%) (Found: C, 71.2; H, 6.65; N, 4.2; S, 9.7. $C_{20}H_{19}NO_2S$ requires C, 71.2; H, 5.65; N, 4.15; S, 9.5%), m/e 337, δ 3.72 (6 H, s); λ_{max} 235 nm.

NN-Di-*p*-tolylbenzenesulphenamide was prepared similarly and purified by column chromatography and crystallization from methanol (60% yield); m.p. 76.5–77.5 °C (Found: C, 78.25; H, 6.05; N, 4.55; S, 10.5. $C_{20}H_{19}NS$ requires C, 78.65; H, 6.25; N, 4.6; S, 10.5%), m/e 305, δ 2.24 (6 H, s), λ_{max} 248 nm.

Reactions of Sulphenamides in Liquid Sulphur Dioxide.—Into a high-pressure vessel containing the sulphenamide (10 mmol), sulphur dioxide (20 ml) was distilled in the dark at –70 °C. The solution was frozen (liquid nitrogen) and evacuated three times at 10^{-5} mmHg, the vessel was allowed to warm to 20 °C, and the reaction was continued for 24 h. After conventional work-up the products were isolated by column chromatography and analysed by n.m.r., i.r., and mass spectroscopy.

*Reaction of NN-Bis-*p*-methoxyphenylbenzenesulphenamide (1) with Aniline in Sulphur Dioxide.*—A mixture of (1) (207 mg, 0.61 mol) and aniline (180 mg, 2 mmol) in liquid sulphur dioxide (20 ml) was kept at room temperature for 24 h. The products were isolated by column chromatography on basic alumina (elution with light petroleum and then light petroleum–ether). Diphenyl disulphide (36.4 mg, 53%), benzenesulphenamide (57.2 mg, 46%), bis-*p*-methoxyphenylamine (129 mg, 93%), and aniline were isolated, and were characterized by comparing physical data with those of authentic samples.

*Reaction of Tetrakis-*p*-methoxyphenylhydrazine (7) with Aniline in Liquid Sulphur Dioxide.*—Into a solution of (7) (684 mg, 1.5 mmol) and aniline (270 mg, 3.0 mmol) was

distilled sulphur dioxide (15 ml) at –70 °C. The mixture was kept at room temperature for 24 h. After conventional work-up, products were isolated by column chromatography.

N-p-Methoxyphenyl-*N'*-phenyl-*p*-phenylenediamine (8) (43.5 mg, 10%), m.p. 125–127 °C (lit.¹⁹ 125–126 °C) (Found: C, 78.35; H, 6.05; N, 9.75. $C_{19}H_{18}N_2O$ requires C, 78.6; H, 6.25; N, 9.65%), m/e 290, δ 3.68 (3 H, s), ν_{max} 3 420, 820, 750, and 700 cm^{-1} , was isolated, along with bis-*p*-methoxyphenylamine (85%).

Photolysis and Thermolysis of Sulphenamides.—A Halos PIH 300 W high-pressure lamp was used as light source. A solution of the sulphenamide (20 mmol) in *n*-pentane (300 ml) was irradiated for 2 h in nitrogen.

Thermolysis of the sulphenamide (20 mmol) was performed at 202 °C in *N*-methyl-2-pyrrolidone (40 ml) for 1 h, while a current of nitrogen was bubbled through.

Products.—2-(*p*-Methoxyanilino)-5-methoxyphenyl phenyl sulphide (3) was a liquid (Found: C, 70.85; H, 5.5; N, 4.3; S, 9.8. $C_{20}H_{19}NO_2S$ requires C, 71.2; H, 5.65; N, 4.15; S, 9.5%), m/e 337, δ 3.72 (6 H, d) and 6.1br (1 H, s), ν_{max} 3 400, 830, 740, and 695 cm^{-1} . 2-(*p*-Tolylamino)-5-methylphenyl phenyl sulphide was a liquid (Found: C, 78.8; H, 6.0; N, 4.75. $C_{20}H_{19}NS$ requires C, 78.65; H, 6.25; N, 4.6%), m/e 305, δ 2.24 (6 H, s) and 6.42 (1 H, s), ν_{max} 3 400, 815, 745, and 695 cm^{-1} . 2-Methylaminophenyl phenyl sulphide and 4-methylaminophenyl phenyl sulphide were acetylated with acetic anhydride. 2-N-Methylacetamidophenyl phenyl sulphide was a liquid (Found: C, 69.3; H, 5.8; N, 5.45; S, 12.45. $C_{15}H_{15}NOS$ requires C, 70.0; H, 5.85; N, 5.45; S, 12.45%), δ 1.85 (3 H, s) and 3.20 (3 H, s), m/e 257, ν_{max} 1 670, 1 590, 760, 740, and 695 cm^{-1} . 4-N-Methylacetamidophenyl phenyl sulphide was a solid, m.p. 74.0–74.5 °C (from light petroleum), m/e 257, δ 1.89 (3 H, s) and 3.22 (3 H, s), ν_{max} 1 665, 1 595, 745, and 695 cm^{-1} .

[7/498 Received, 21st March, 1977]

¹⁹ F. A. Davis, E. R. Fretz, and C. J. Horner, *J. Org. Chem.*, **1973**, **38**, 690.