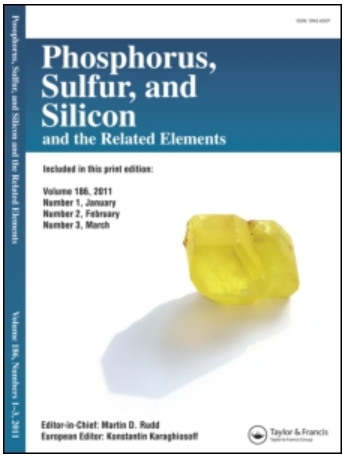

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THE SULPHUR (II)-NITROGEN BOND. PART V.[1] THE REACTION OF *O*-METHYL BENZENESULPHENATE WITH LIQUID AMMONIA

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In contrast to its behaviour with primary and secondary amines, *O*-methyl benzenesulphenate PhSOMe reacts only sluggishly with liquid ammonia. The products thus far characterized are dibenzenesulphenamide $(PhS)_2NH$ **1**, diphenyl disulphide **2**, 1,2-benzoquinone bisphenylthioimine **3** and *N,N*-bis(phenylthio)sulphur diimide **4**.

INTRODUCTION

Gently warming both primary and secondary amines with *O*-methyl benzenesulphenate gives the appropriate sulphenamide in good yield. *N*-Methyl benzenesulphenamide reacts further, excess sulphenate producing *N*-methyl dibenzenesulphenamide.[2] The sulphenate, like sulphenamides, also reacts readily with thiols, particularly thiophenol, to give disulphides.[3]

$$PhSOMe + Pr^n_2NH \longrightarrow PhSNPr^n_2 + MeOH$$

$$PhSNHMe + PhSOMe \longrightarrow (PhS)_2NMe + MeOH$$

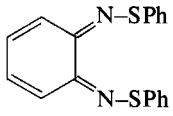
RESULTS AND DISCUSSION

These observations prompt us to report the reaction of excess liquid ammonia with *O*-methyl benzenesulphenate. It is very slow, and after stirring for 6 hr, and allowing the excess liquid ammonia to evaporate, left a pale yellow liquid. This darkened to a deep red colour after 6 days at room temperature and a white crystalline solid was precipitated. Filtration after a further 10 days at 0°C gave dibenzenesulphenamide **1**. No benzenesulphenamide was isolated. A large proportion of the sulphenate was recovered from the filtrate by distillation, and the residue was chromatographed, giving diphenyldisulphide **2**, maroon 1,2-benzoquinone bisphenylthioimine **3** and orange *N,N'*-bis(phenylthio)sulphur diimide **4**.

$$2PhSOMe + NH_3 \longrightarrow (PhS)_2NH + 2MeOH$$

1

Compound **3** was isolated as a crystalline sharp melting solid which, like dibenzenesulphenamide **1**, was characterized by full elemental analysis. The structural formula proposed for **3** is supported by the mass spectrum, which shows a molecular ion, and major peaks at *m/e* 245 ($C_6H_4N_2S_2Ph$), 213 ($C_6H_4N_2SPh$), 136 ($C_6H_4N_2S$) and 109 (C_6H_5S). In addition, the uv spectrum of **3**[λ_{max} 438 nm (ε 12,600) and 510 nm (ε 13,500)] closely resembles that of the dimethyl homologue 3,5-dimethyl-1,2-benzoquinone bisphenylthioimine **5** [λ_{max} 435 nm (ε



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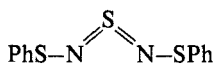

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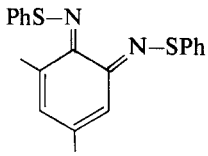

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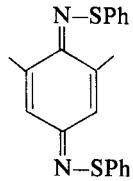

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9700) and 500 nm (ε 13,200)] and not its 2,6-dimethyl-1,4-benzoquinone isomer **6**[λ_{max} 468 nm (ε 47,500) and 280 nm (ε 13,100)]. These dimethyl isomers have been obtained by reaction of the appropriate dimethyl aniline with tribenzenesulphenamide, whereas aniline itself yielded only an intractable mixture.[4]

The structure proposed for the sulphur diimide **4** was supported by full elemental analysis, and by its mass spectrum which showed a strong molecular ion, and major peaks at *m/e* 200 ($C_6H_4N_2S_3$), 154 ($C_6H_4S_2N$), 123 (C_6H_5SN) and 109 (C_6H_5S). The formulation has been confirmed by an x-ray structure determination.[5]

It seems likely that **3** is formed from the interaction of $(PhS)_2N$ radicals with some phenylthio derivatives. These radicals may well be formed slowly by the air oxidation of dibenzenesulphenamide, or the daylight photolysis of the tribenzenesulphenamide so formed. Lead dioxide is reported to give a purple colour[6] with $(PhS)_2NH$ **1**, the solution yielding $(PhS)_3N$ which itself can be photolysed to give a purple solution yielding **1**.[4] The absence of any intense purple colour in our reaction implies slow formation, and immediate reaction of this radical, with thiophenol for example. Thiophenol could result from nucleophilic attack by ammonia at the methyl protons of the sulphenate ester. Corresponding behaviour has been observed with methanesulphenyl chloride, which undergoes extensive deprotonation in dimethylamine.[7]

$$Me_2NH + MeSCl \longrightarrow Me_2NH_2^+ + CH_2S + Cl^-$$

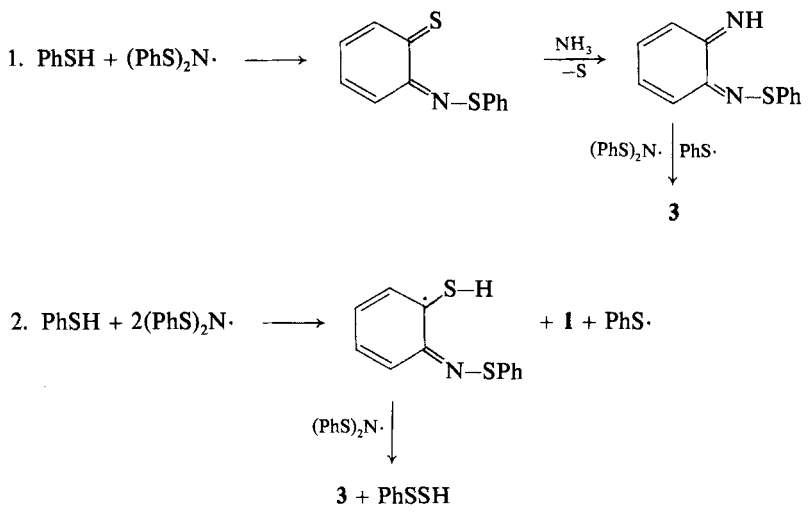
$$NH_3 + MeOSPh \longrightarrow NH_4^+ + CH_2 + PhS^-$$

Although thiophenol so generated is very likely to react with the excess sulphenate ester,[3] this does not exclude the possibility that the small quantities of **3** and **4** isolated arise from the reaction of the small concentrations of $(PhS)_2N$ radicals with thiophenol. Two pathways suggest themselves and both generate sulphur, either from the thioquinone or from phenyl hydrodisulphide, through interaction with ammonia[8] (Scheme 1). The direct interaction of sulphur with the amide radicals will then produce the sulphur diimide **4**. Compound **4** is also formed directly by irradiating sulphur and tribenzenesulphenamide.[9] It is therefore reasonable to suppose that **4** results directly from the sulphur generated through the formation of **3**.

$$2(PhS)_2N\cdot + S \longrightarrow PhS{-}N\overset{S}{\diagup\!\!\diagdown}N{-}SPh + Ph_2S_2$$

4

None of the *para*-isomer of **3** was detected. This is not surprising since ortho substitution of phenols with tribenzenesulphenamide is reported to predominate.[4] Likewise, the synthesis of selenium analogues using diphenylseleninic anhydride and hexamethyldisilazane with phenols results in less than 10% of the *para*-isomer being formed.[10]



SCHEME 1

EXPERIMENTAL SECTION

O-Methyl benzenesulphenate (5.1 g) was added to an excess of liquid ammonia and stirred at between −80°C and −33°C for 6 hr. The excess ammonia was allowed to vaporize away leaving a pale yellow liquid. This was kept at room temperature for 6 days. During this period it darkened to a deep red colour and precipitated colourless crystals. The mixture was left for a further 10 days in the refrigerator, then filtered, and washed with pentane to give dibenzenesulphenamide **1**, $(PhS)_2NH$ as pale pink crystals, which darkened at 125° and melted at 127–8° (lit: 129°),[6] yield 0.160 g (Analysis. Calc. for $C_{12}H_{11}NS_2$: C, 61.9; H, 4.72; N, 6.02; S, 27.5%. Found: C, 61.5; H, 4.63; N, 6.05; S, 27.0%). The pentane and excess sulphenate (3.0 gm, bp 50°/9 mm, n_D^{21} 1.5625) was distilled from the coloured filtrate and the residue chromatographed using benzene/30–40° petrol (ratio 1:9) as eluant. Three crystalline products were characterized. Diphenyl disulphide **2** eluted just behind the solvent front (R_F 0.95) as a pale yellow band, mp 59° (infrared spectrum identical with an authentic sample). This was followed by an orange-red band (R_F 0.50) and a maroon band (R_F 0.38) which on extraction yielded **4** and **3** respectively in low yield (less than 10 mg of each).

Compound **4** was characterized as *N,N'*-bis(phenylthio)-sulphur diimide, mp 107–8° (lit: 105°)[11] (Analysis. Calc. for $C_{12}H_{10}N_2S_3$: C, 51.7; H, 3.6; N, 10.1; S, 34.5%. Found: C, 51.3; H, 3.8; N, 10.1; S, 34.7%). The mass spectrum shows *m/e* 278 (41), 200 (28), 154 (55), 123 (41) and 109 (100). An x-ray structure determination confirmed the structure proposed for **4**.[5]

Compound **3** was characterized as 1,2-benzoquinone bis-phenylthioimine, mp 74–5° (Analysis. Calc. for $C_{18}H_{14}N_2S_2$: C, 67.1; H, 4.4; N, 8.7; S, 19.9%. Found: C, 67.2; H, 4.6; N, 8.0; S, 19.2%). The mass spectrum shows *m/e* 322 (5), 245 (5), 213 (100), 136 (8) and 109 (84). The uv spectrum of **3**[λ_{max} 438 nm (ε 12,600) and 510 nm (ε 13,500)] was compared with those of 3,5-dimethyl-1,2-benzoquinone bisphenylthioimine **5**[λ_{max} 435 nm (ε 9700) and 500 nm (ε 13,200)] and the 2,6-dimethyl-1,4-benzoquinone isomer **6** [λ_{max} 468 nm (ε 47,500) and 280 nm (ε 13,100)].[4]

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