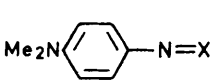
Preparation and Properties of *p*-Dimethylamino-*N*-thiosulphinylaniline

By **Derek H. R. Barton** * and **Michael J. Robson**, Department of Chemistry, Imperial College, London SW7 2AY

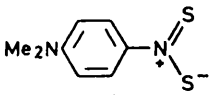
p-Dimethylamino-*N*-thiosulphinylaniline has been prepared in several different ways, most conveniently by the action of phosphorus pentasulphide on *NN*-dimethyl-*p*-nitrosoaniline. The properties of this compound, containing the new functional group –N=S=S, have been studied briefly.

In connection with another investigation we had need to study the properties of the thionitroso-group (–N=S). There is little mention of compounds containing this group in the literature,[1,2] and they appear to be unstable.

An aromatic thionitroso-compound with an electron-donating *para*-substituent appeared the most likely to be stable. The obvious choice was 1-dimethylamino-4-thionitrosobenzene (I; X = S), to be prepared by replacing the oxygen in (I; X = O) by sulphur. Treatment of *NN*-dimethyl-*p*-nitrosoaniline (I; X = O)



(I)



(II)

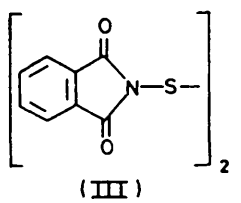
with phosphorus pentasulphide in methylene chloride–pyridine at 24—32° gave a crystalline purple compound of the unexpected formula $C_8H_{10}N_2S_2$. The molecular weight was determined both by osmometry and by mass spectrometry. Reduction with sodium borohydride or hydrogen sulphide, or acidic hydrolysis, gave *NN*-dimethyl-*p*-phenylenediamine (I; X = H_2), thus showing that four aromatic hydrogen atoms were still present. This was confirmed by the proton n.m.r. spectrum. Clearly the purple compound must be either *p*-dimethylamino-*N*-thiosulphinylaniline (I; X = S=S) or *p*-dithionitro-*NN*-dimethylaniline (II).

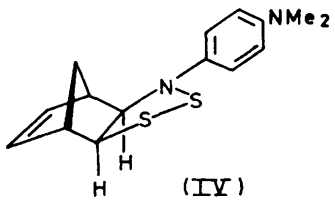
The former structure (I; X = S=S) was established by the following alternative methods of synthesis. Treatment of *p*-dimethylamino-*N*-sulphinylaniline [3] with phosphorus pentasulphide gave the purple compound. Similarly, the reaction of *NN*-dimethyl-*p*-phenylenediamine (I; X = H_2) with disulphur dichloride or with diphthalimido disulphide [4] (III) gave the same material,

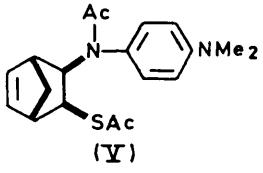
[1] P. Tavs, *Angew. Chem. Internat. Edn.*, 1966, **5**, 1048.
[2] W. J. Middleton, *J. Amer. Chem. Soc.*, 1966, **88**, 3842.
[3] G. Kresze and A. Maschke, *Chem. Ber.*, 1961, **94**, 450.
[4] M. V. Kalnins, *Canad. J. Chem.*, 1966, **44**, 2112.

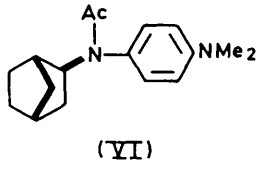
as judged by the characteristic visible and u.v. spectrum. The reactions recorded below also define the structure as (I; X = S=S).

The purple compound reacted smoothly with norborna-2,5-diene to furnish a crystalline adduct, the n.m.r. spectrum of which showed, besides the signal at τ 3·75 due to two olefinic protons, two one-proton signals due to tertiary protons next to sulphur or nitrogen [τ 5·63 (broad doublet) and 6·08 and 6·13 (pair of doublets)]. The difference in shift of these two signals shows at once that the adduct cannot be derived from the dithionitro-compound (II). Spin-decoupling experiments showed that the two one-proton signals both exhibited coupling (*J ca.* 2 Hz) with the *anti*-bridge proton and that they must both, therefore, be *endo*.[5] Hence the adduct must have the structure (IV). This is in agreement with previous findings that 1,3-dipolar reagents add to norbornadiene exclusively or predominantly from the *exo*-direction.[6]


(III)

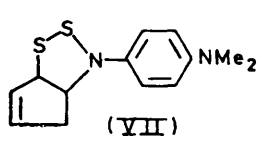

(IV)

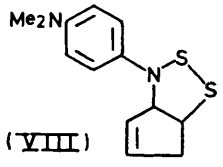

(V)


(VI)

Reduction of the adduct (IV) with lithium aluminium hydride followed by acetylation gave an *NS*-diacetyl derivative (V), as shown by the analytical figures and by spectral data. Treatment of the adduct (IV) with Raney nickel afforded, after acetylation, the saturated tertiary amide (VI).

1,3-Dipolar addition of the thiosulphinylamine (I; X = S=S) to olefins is probably a general reaction. Thus, a smooth reaction with cyclopentadiene gave a crystalline 1 : 1 adduct to which we assign the constitution (VII) or (VIII) or an equivalent structure.


(VII)


(VIII)

Pyrolysis of the thiosulphinylamine (I; X = S=S) at 200° gave *pp'*-bisdimethylaminoazobenzene and sulphur.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were recorded on a Unicam SP 200 spectrometer and u.v. spectra with a Unicam SP 800B instrument. ^{1}H N.m.r. spectra were recorded with a Varian T60 spectrometer (tetramethylsilane as a internal reference). Mass spectra were recorded with an A.E.I. MS9 or a Perkin-Elmer 270 machine.

Unless otherwise stated: (*a*) all reactions and work-up procedures were carried out at room temperature; (*b*) solvents were removed under reduced pressure with minimum heating; (*c*) solutions in organic solvents were dried with anhydrous sodium sulphate (when necessary).

Neutral, grade III alumina was used for column chromatography. Petroleum refers to the fraction boiling at 60—80°. ' Light petroleum ' refers to the 40—60° fraction.

p-*Dimethylamino*-N-*thiosulphinylaniline*.—To *NN*-dimethyl-*p*-nitrosoaniline (12 g) in benzene (150 ml) and methylene chloride (60 ml) was added phosphorus pentasulphide (13·5 g). To the rapidly stirred suspension *under nitrogen* was added *dry* pyridine (60 ml) over 13 min. With the temperature maintained between 24 and 32°, the mixture was stirred *under nitrogen* and the reaction was monitored by t.l.c. (silica; ethyl acetate). As soon as the starting nitrosoaniline had disappeared (*ca.* 35 min.), the deep violet mixture was poured slowly *under nitrogen* into a vigorously stirred mixture of light petroleum (1·26 l) and methylene chloride (270 ml). The flask was washed out with methylene chloride (3 × 20 ml) and the washings were added, under nitrogen, to the petroleum–methylene chloride mixture. This was then stirred under nitrogen for 5 min, and shaken vigorously for a further 2 min, to ensure thorough extraction of the product. The mixture was immediately filtered through Celite 545 and the solvent was removed from the filtrate with heating to 40° maximum. The pyridine-free, solid residue was extracted with boiling petroleum (1 × 650 ml; 1 × 300 ml) and the extracts were cooled to 0°. The cold mixtures were filtered giving p-*dimethylamino*-N-*thiosulphinylaniline* as deep violet needles (15%), m.p. 113—115° (slow decomp.), $\nu_{max.}$ (Nujol) 1605, 1535, 1315, 1290, 1180, 830, and 680 cm^{-1} $\lambda_{max.}$ (MeOH) 238sh (ε 4600), 262sh (5900), 285 (7200), 350 (1700), and 538 (ε 39,000) nm, $\lambda_{max.}$ (C_6H_{12}) 255 (ε 7400), 284 (7100), 348 (3300), and 510 (38,400) nm, τ ($CDCl_3$) 6·9 (6H, s), 3·35 (2H, d), and 1·4 (2H, d), *m/e* 198 (M^+), *M* (osmometric, in chloroform) 213 (average of two values) (Found: C, 48·4; H, 5·1; N, 14·1; S, 32·55. $C_8H_{10}N_2S_2$ requires C, 48·5; H, 5·1; N, 14·15; S, 32·3%).

Reduction of p-*Dimethylamino*-N-*thiosulphinylaniline with Sodium Borohydride*.—To the thiosulphinylamine (100 mg) in tetrahydrofuran (10 ml) was added sodium borohydride (200 mg) and the mixture stirred until the purple colour had been complete discharged (*ca.* 10 min). After filtration, the solvent was removed and to the residue in chloroform (10 ml) at 0° were added triethylamine (90 mg) and, dropwise, benzoyl chloride (70 mg) in chloroform (2 ml). The solvent was removed and the product washed with a little ether and extracted with boiling benzene (3 × 10 ml). The extracts were cooled and filtered to give white needles of *N'*-benzoyl-*NN*-dimethyl-*p*-phenylenediamine (50%), m.p. and mixed m.p. 227—228°.

Reaction of p-*Dimethylamino*-N-*sulphinylaniline with Phosphorus Pentasulphide*.—To the sulphinylamine (I;

[5] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1171, and references cited therein.

[6] *Inter alia*. M. R. Brinkman and C. W. Allen, *J. Amer. Chem. Soc.*, 1972, **94**, 1550; A. C. Ocheschlager and L. H. Zalkow, *J. Org. Chem.*, 1965, **30**, 4205; A. G. Anastassiou, *ibid.*, 1966, **31**, 1131; S. McLean and D. M. Findlay, *Tetrahedron Letters*, 1969, **27**, 2219; R. R. Fraser and Y. S. Lin, *Canad. J. Chem.*, 1969, **46**, 801.

X = S=O) (0·50 g) in benzene (50 ml) was added phosphorus pentasulphide (4·5 g) and the mixture was stirred under nitrogen for 16 h. More pentasulphide (1·0 g) was added and the mixture stirred for a further 10 h. The mixture was added with stirring under nitrogen to petroleum (150 ml) and the resulting suspension filtered through Celite 545. The solvent was removed from the filtrate and the residue was extracted with boiling petroleum (50 ml). The cooled extract was filtered to give *p*-dimethylamino-*N*-thiosulphinylaniline (I; X = S=S) (7·3 mg), m.p. 110—115°.

Reaction of p-*Dimethylamino*-N-*thiosulphinylaniline with Norbornadiene.*—To the thiosulphinylamine (1·0 g) in methylene chloride (30 ml) was added freshly redistilled norbornadiene (15·8 g) and the solution was kept in the dark for 50 h. The solvent was removed and the residue was purified by column chromatography on alumina (benzene). The first yellow fraction was collected and the solvent removed giving the crude, crystalline 1 : 1 adduct, 3-p-*dimethylaminophenyl*-3a,4,7,7a-*tetrahydro*-4,7-*methano*-3H-1,2,3-*benzodithiazole* (IV) (62%). Two recrystallisations from light petroleum gave a sample of m.p. 118—119° (decomp.), τ ($CDCl_3$) 8·45br (1H, d), 7·2 (3H, s), 6·8—7·2 (3H, s), 6·13 (d, *J ca.* 2 Hz) and 6·08 (d, *J ca.* 2 Hz) (1H), 5·63br (1H, d), 3·75br (2H, s), 3·45 (2H, d), and 2·95 (2H, d) (irradiation of the signal at τ 8·45 caused the doublets at τ 6·13 and 6·08 to collapse to singlets, and the doublet at τ 5·63 to be sharpened), *m/e* 290 (M^+) (Found: C, 62·1; H, 6·1; N, 9·45; S, 21·8. $C_{15}H_{18}N_2S_2$ requires C, 62·05; H, 6·25; N, 9·65; S, 22·05%).

Reduction of the Norbornadiene Adduct with Lithium Aluminium Hydride.—To the adduct (IV) (2 mmol) in tetrahydrofuran under nitrogen was added, in small portions, with stirring, lithium aluminium hydride (10 mmol), and the mixture was stirred for 30 min. Ethyl acetate (5 ml) and acetyl chloride (3·71 g) were added slowly to the mixture which was stirred for 30 min and filtered. The solvent was removed and the residue taken up in ethyl acetate (30 ml), and the solution was extracted with *ca.* 0·7N-hydrochloric acid (45 ml). The extract was neutralised with saturated aqueous sodium bicarbonate and extracted with ethyl acetate (50 ml). The solvent was removed from the extract and the residue crystallised from benzene–petroleum to give the crude S-[3-exo(N-*acetyl*-p-*dimethylaminoanilino*)*norborn*-5-*en*-2-exo-*yl*] *thioacetate* (V) as a fawn solid (45%), m.p. 148—151°. Chromatography on alumina (ethyl acetate), followed by two recrystallisations from petroleum afforded a sample of m.p. 151—152°, $\nu_{max.}$ (Nujol) 1680 and 1655 cm^{-1}, τ ($CDCl_3$) 8·7br (2H, s), 8·2 (3H, s), 7·6 (3H, s), 7·4br (1H, s), 7·2br (1H, s), 7·0 (3H, s), 6·05br (1H, d), 5·5br (1H, d), 3·8 (2H, m), and 2·4—3·5 (4H, m) (Found: C, 66·25; H, 6·95; N, 8·0; S, 9·25. $C_{19}H_{24}N_2O_2S$ requires C, 66·25; H, 7·0; N, 8·15; S, 9·3%).

N-(p-*Dimethylaminophenyl*)*norbornan*-2-exo-*amine.*— To the norbornadiene adduct (IV) (0·50 g) in ethyl acetate (40 ml) was added Raney nickel (W-4; 12·0 g) suspended in ethyl acetate (10 ml). The mixture was stirred for 2 h, then centrifuged, and the supernatant liquid was decanted. The Raney nickel was stirred for 15 min with ethyl acetate (50 ml) and the mixture was subjected to centrifugation and decantation. Removal of the solvent from the combined solutions gave an oil which solidified to give the amine as a waxy solid (46%), m.p. 40—44°, $\nu_{max.}$ (film) 3400, 2980, and 1540 cm^{-1}, *m/e* 230 (M^+).

N-(p-*Dimethylaminophenyl*)-N-(*norbornan*-2-exo-*yl*)*acetamide* (VI).—To the crude norbornanamine (180 mg) in chloroform (10 ml) were added triethylamine (220 mg) and acetyl chloride (133 mg). The mixture was washed with aqueous 4N-sodium hydroxide and water, and the solvent was removed to give the crystalline amide (86%). Column chromatography on alumina (*ca.* 10 g) (ethyl acetate), followed by two recrystallisations from petroleum afforded white *needles*, m.p. 114—116°, $\nu_{max.}$ (Nujol) 1650, 1610, and 1530 cm^{-1}, τ ($CDCl_3$) 9·2br (2H, s), 8·1—9·0 (6H, m), 8·2 (3H, s), 9·2br (2H, s), 8·1—9·0 (6H, m), 8·2 (3H, s), 7·85 (2H, m), 7·0 (3H, s), 5·5br (1H, t), and 2·8—3·3 (4H, m) (Found: C, 75·2; H, 8·75; N, 10·2. $C_{17}H_{24}N_2O$ requires C, 74·95; H, 8·9; N, 10·3%).

Addition of p-*Dimethylamino*-N-*thiosulphinylaniline to Cyclopentadiene.*—To the thiosulphinylamine (0·50 g) in methylene chloride (25 ml) under nitrogen at 0° was added freshly prepared cyclopentadiene (7·0 g). The solution was kept in the dark at 4° for 74 h, the solvent was removed with minimum heating, and the residue was chromatographed on alumina (benzene). Removal of the solvent from the first (pale) yellow fraction gave the crude crystalline 1 : 1 adduct (78%). Four recrystallisations from light petroleum furnished a sample of m.p. 79·5—80·5°, $\nu_{max.}$ (Nujol) 1615 and 1525 cm^{-1}, *m/e* 264 (M^+) (Found: C, 59·35; H, 6·15; N, 10·5; S, 24·45. Calc. for $C_{13}H_{16}N_2S_2$: C, 59·1; H, 6·1; N, 10·6; S, 24·2%).

Pyrolysis of p-*Dimethylamino*-N-*thiosulphinylaniline.*—The thiosulphinylamine (100 mg) was heated under nitrogen to 200° for 10 min, and the product was chromatographed on alumina (methylene chloride). The first orange fraction was collected and the solvent removed to give 4,4′-bisdimethylaminoazobenzene (74 mg), slightly contaminated with sulphur.

Hydrolysis of p-*Dimethylamino*-N-*thiosulphinylaniline.*—To the thiosulphinylamine (50 mg) in diethyl ether (20 ml) was added aqueous 2N-hydrochloric acid (2 ml) and the mixture was shaken until a deep violet colour appeared in the aqueous layer. An excess of saturated aqueous sodium bicarbonate was added and the phases were separated. Half the solvent was removed from the ethereal layer and to the remaining solution were added triethylamine (*ca.* 50 mg) and benzoyl chloride (*ca.* 60 mg). The precipitate was filtered off and extracted with boiling benzene (10 ml), and the extract was cooled to precipitate *N′*-benzoyl-*NN*-dimethyl-*p*-phenylenediamine (16·4 mg).

Reaction of p-*Dimethylamino*-N-*thiosulphinylaniline with Hydrogen Sulphide.*—Hydrogen sulphide was passed for 5 min through the thiosulphinylamine (575 mg) in methylene chloride (20 ml) and diethyl ether (50 ml). The solution was kept for 2 days in a stoppered flask, and the solvent was then removed. Methylene chloride (20 ml) was added to the residue and the mixture was filtered. To the filtrate cooled in ice, pyridine (300 mg) was added, followed by benzoyl chloride (438 mg) in methylene chloride (2 ml). The solvent was removed from the unfiltered mixture, the residue was boiled with chloroform (25 ml), and the mixture was cooled. Filtration gave *N′*-benzoyl-*NN*-dimethyl-*p*-phenylenediamine (73%).

We thank the S.R.C. for a C.A.P. Studentship sponsored by Messrs. Albright and Wilson.

[4/173 *Received, 29th January,* 1974]