Fenton's Reagent in Dimethyl Sulphoxide: an Unusual Sulphonylating System. X-Ray Crystallographic Analysis of 4-*N*,*N*-Dimethylamino-*N*,*N*-dimethanesulphonylaniline

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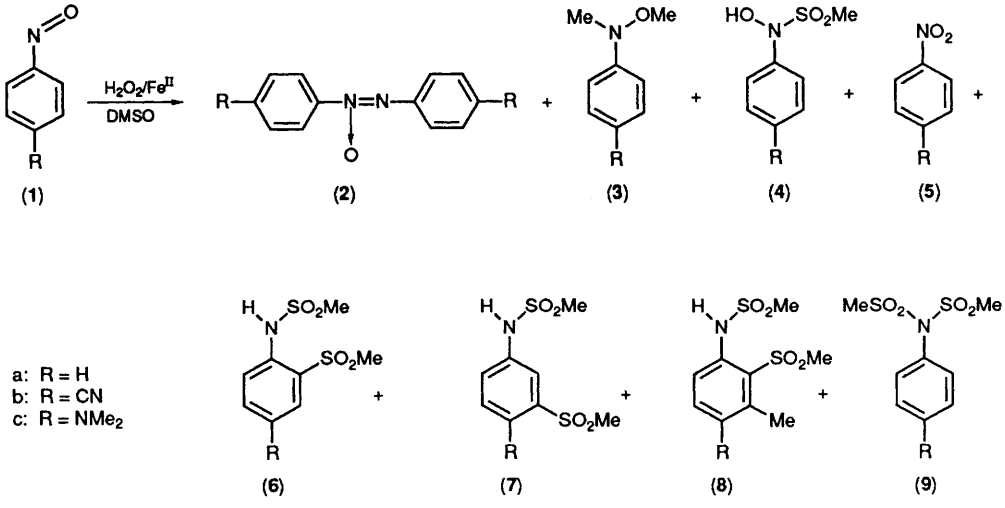
On treatment with Fenton's reagent in dimethyl sulphoxide nitrosoarenes form sulphonylate products, while the expected *N*,*O*-dimethylated hydroxylamine is isolated only in the case of nitrosobenzene in low yield. Nitrosobenzene and 4-cyanonitrosobenzene lead to *N*-sulphonylhydroxylamines while 4-nitroso-*N*,*N*-dimethylaniline and 1-nitroso-2-phenyl-3-acetylindolizine give sulphonamides and ring-sulphonylated products. A nitrenium cation is suggested to play a primary role in this process. X-Ray analysis of the title compound confirms the trigonal planar arrangement of the dimethylamino group and its coplanarity with the benzene ring, as expected in accord with the results found in related derivatives.

The reaction of dimethyl sulphoxide (DMSO) with the redox system H_2O_2/Fe^{II} provides an efficient source of methyl radical,[1] a typical application of this reaction being the methylation of protonated *N*-heteroaromatic bases.[1,2] It is well known that the reaction of alkyl radicals with nitroso derivatives generally leads to nitroxide radicals,[3] which in turn may couple with other alkyl radicals to afford alkylated hydroxylamines.[4,5] On this basis it seemed to us worthwhile attempting the preparation of *N*,*O*-dimethylated hydroxylamines by reaction of Fenton's reagent with nitroso compounds in DMSO.

We therefore carried out the reaction of nitrosobenzene (**1a**), 4-cyanonitrosobenzene (**1b**), 4-nitroso-*N*,*N*-dimethylaniline (**1c**) and 1-nitroso-2-phenyl-3-acetylindolizine (**10**) with H_2O_2/Fe^{II} in DMSO, but only compound (**1a**) led to a small amount of the expected *N*,*O*-dimethylated hydroxylamine. In all cases sulphonyl hydroxylamines, sulphamides and sulphones were obtained, although the products identified accounted for only 40% of the starting nitroso compound.

Results

In a typical run, the nitroso compound was dissolved in DMSO and treated with 40% H_2O_2 and $FeSO_4 \cdot 7H_2O$ in a 1:3:0.2 molar ratio. The reaction mixture was then chromatographed on SiO_2 and the products purified by TLC. Nitrosobenzene (**1a**) afforded azoxybenzene (**2a**) (13%), the expected *N*,*O*-dimethylhydroxylamine (**3a**) (16%) and the sulphonylhydroxylamine (**4a**) (11%). While compound (**2a**) was identified by comparison with an authentic sample, (**3a**) was characterized through mass and NMR spectra: typical singlets at δ 2.81 and 3.88 were observed for the NMe and OMe protons, respectively. As regards (**4a**), its mass and IR (intense band at 3 340 cm^{-1}) spectral identification was substantiated by the fact that, when dissolved in chloroform, it could be readily oxidized with PbO_2 to the sulphonylarylnitroxide (**13a**) which was characterized by means of ESR spectroscopy [a_N 11.77, a_H(3 H) 2.02, a_H(2 H) 0.83, a_H(3 H) 0.42 G, g = 2.0056], its spectral parameters having been found to be consistent with those reported for other arylsulphonylnitroxides.[6]



(1) (2) (3) (4) (5) (6) (7) (8) (9)

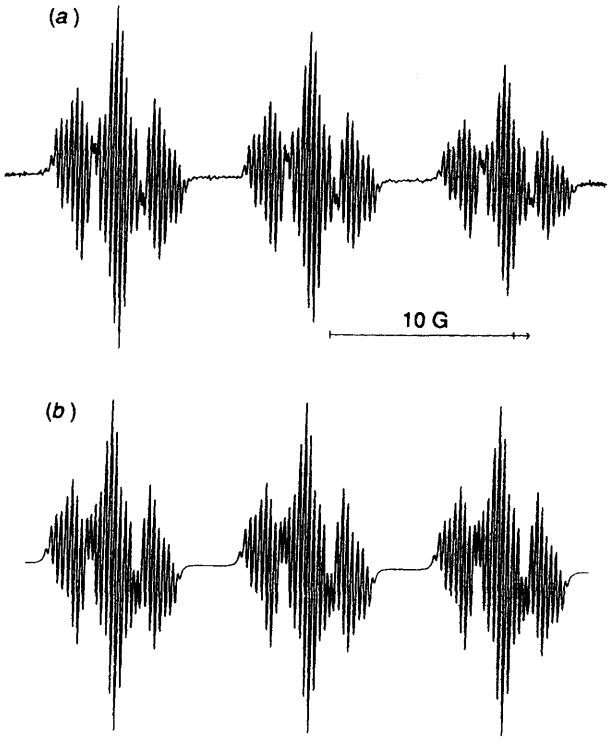
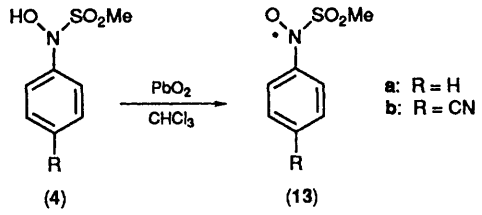


Figure 1. ESR spectrum of (**13a**) recorded at room temperature: (*a*) experimental; (*b*) computer simulated with a line width of 0.15 G.

From the reaction of 4-cyanonitrosobenzene (**1b**) only compounds (**2b**) and (**4b**) could be isolated. The 4,4′-dicyanoazoxybenzene (13%) was again identified by comparison with authentic samples, while the *N*-methanesulphonylhydroxylamine (31%) was characterized by mass, IR, and NMR spectroscopy (singlet at δ 2.96 for SO_2Me and *pseudo*-quartet at δ 7.80 for the A_2B_2 aromatic protons). Again, treatment of (**4a**) with PbO_2 in chloroform led to the methanesulphonylaryl-



nitroxide (**13d**), whose ESR spectral parameters [a_N 10.87, a_H(2 H) 2.17, a_H(2 H) 0.88, a_N 0.26, a_H(3 H) 0.28 G, g = 2.0056] were consistent with those determined for (**13a**) (see Figure 1).

Six different products were isolated from the reaction of 4-nitroso-*N*,*N*-dimethylaniline: 4,4′-(*N*,*N*-dimethylamino)azoxybenzene (**2c**) (11%) and 4-nitro-*N*,*N*-dimethylaniline (**5c**) (9.6%) were identified by comparison with authentic samples. The characterization of the isomeric compounds (**6c**) (9.2%) and (**7c**) (7.2%), as well as of compound (**8c**) (3.9%) could not be based on their IR and NMR spectral properties alone, because of the problem created by the presence of two methanesulphonylic groups in their molecules; their conformation was however completely elucidated by the X-ray structural analysis published elsewhere.[7] The NMR spectrum of compound (**9c**) (4.3%) exhibited two singlets at δ 2.86 (*N*,*N*-dimethylamino group) and at δ 3.24 (the two methanesulphonyl groups) and an A_2B_2 system centred at δ 6.79 due to the four aromatic protons; owing to the uncertainty about the molecular ion

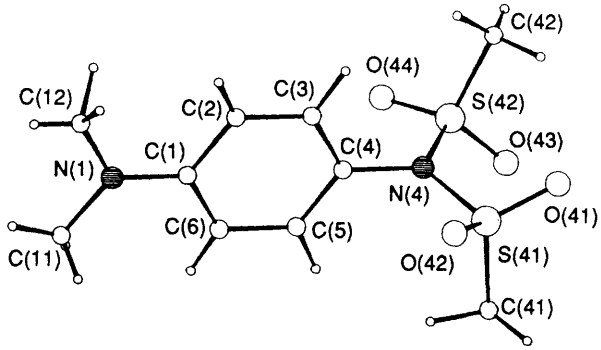
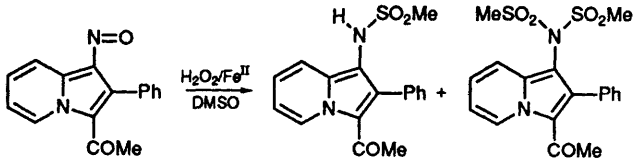


Figure 2. Perspective view of 4-*N*,*N*-dimethylamino-*N*,*N*-dimethanesulphonyl aniline (**9c**).

peak in the mass spectrum, its structure was determined by the X-ray analysis reported in this paper.

The reaction of nitrosoindolizine (**10**) with Fenton's reagent led to the compounds (**11**) (12%) and (**12**) (7.4%), identified from NMR spectroscopy and mass spectra.



Compound (**11**) shows a main peak at mass $M - SO_2Me$, while compound (**12**) shows two main peaks at mass $M - SO_2Me$ and $M - 2SO_2Me$, as expected from the structures proposed. For compound (**11**) the NMR signals of COMe and SO_2Me fall at δ 2.0 and 2.45, respectively, while for the disulphonamide (**12**) the signals fall at δ 1.98 (3 H, from COMe) and 3.1 (6 H from SO_2Me).

Compounds (**4b**), (**6c**)–(**9c**), (**11**) and (**12**) all exhibited in their IR spectra an absorption at *ca.* 1 150 cm^{-1}, typical of the SO_2Me moiety.

Molecular Geometry of (**9c**).—Bond distances and angles and selected torsion angles are reported in Table 1; the arbitrary numbering scheme used in the crystal analysis is shown in Figure 2, which represents a perspective view of the molecule.

Geometrical parameters in the dimethylamino moiety show a configuration around the N(1) atom which is very similar to that found in 2-methanesulphonyl-4-(*N*,*N*-dimethylamino)-methanesulphanilide, previously studied,[7] in which there are no *ortho*-substituents at the phenyl group. In fact, the N angles [C(1)–N(1)–C-(11) 120.5(4), C(1)–N(1)–C(12) 121.9(4), C(11)–N(1)–C(12) 117.6(4)°] confirm the trigonal planar arrangement of the dimethylamino group, as well as the pyramidality of N(1), the distance of this atom from the C(1), C(11), C(12), plane being 0.008 Å. In related compounds already described,[7] it has been remarked that deviations from coplanarity of the C(11)–N(1)–C(12) group with respect to the benzene ring are vanishingly small in the absence of steric hindrance; in the present structure, in the absence of intra- or inter-molecular short contacts or hydrogen bonds, the dihedral angle between their mean planes is 2.1(2)°. In contrast to that expected, the geometry around N(4) is significantly deviated from the trigonal planar arrangement, the N(4) atom being 0.057(2) Å out of the plane through C(4), S(41), S(42). The orientation of the two methanesulphonyl groups with respect to the benzene ring, deduced from the torsion angles reported in Table 1, is the same; the dihedral angle formed by the mean

Table 1. Bond distances/Å, angles/° and selected torsion angles/° with esds in parentheses.

Bond distances			
S(41)–O(41)	1.420(4)	N(1)–C(11)	1.455(6)
S(41)–O(42)	1.421(4)	N(1)–C(12)	1.426(6)
S(41)–N(4)	1.670(3)	N(4)–C(4)	1.453(5)
S(41)–C(41)	1.756(5)	C(1)–C(2)	1.413(4)
S(42)–O(43)	1.427(4)	C(1)–C(6)	1.384(5)
S(42)–O(44)	1.421(3)	C(2)–C(3)	1.378(5)
S(42)–N(4)	1.687(3)	C(3)–C(4)	1.376(5)
S(42)–C(42)	1.745(4)	C(4)–C(5)	1.375(4)
N(1)–C(1)	1.376(5)	C(5)–C(6)	1.399(5)
Bond angles			
O(41)–S(41)–O(42)	119.3(2)	C(11)–N(1)–C(12)	117.6(4)
O(41)–S(41)–N(4)	106.7(2)	S(41)–N(4)–S(42)	120.4(2)
O(41)–S(41)–C(41)	110.0(3)	S(41)–N(4)–C(4)	119.9(2)
O(42)–S(41)–N(4)	106.3(2)	S(42)–N(4)–C(4)	119.3(2)
O(42)–S(41)–C(41)	108.6(2)	N(1)–C(1)–C(2)	120.1(3)
N(4)–S(41)–C(41)	105.0(2)	N(1)–C(1)–C(6)	122.4(3)
O(43)–S(42)–O(44)	118.5(2)	C(2)–C(1)–C(6)	117.5(3)
O(43)–S(42)–N(4)	107.9(2)	C(1)–C(2)–C(3)	120.8(3)
O(43)–S(42)–C(42)	109.4(3)	C(2)–C(3)–C(4)	120.4(3)
O(44)–S(42)–N(4)	106.1(2)	N(4)–C(4)–C(3)	120.1(3)
O(44)–S(42)–C(42)	109.5(2)	N(4)–C(4)–C(5)	119.7(3)
N(4)–S(42)–C(42)	104.5(2)	C(3)–C(4)–C(5)	120.2(4)
C(1)–N(1)–C(11)	120.5(4)	C(4)–C(5)–C(6)	119.7(3)
C(1)–N(1)–C(12)	121.9(4)	C(1)–C(6)–C(5)	121.4(3)
Torsion angles			
O(41)–S(41)–N(4)–C(4)	−154.6(3)	C(42)–S(42)–N(4)–C(4)	106.4(3)
O(42)–S(41)–N(4)–C(4)	−26.4(3)	C(11)–N(1)–C(1)–C(6)	−3.1(6)
C(41)–S(41)–N(4)–C(4)	88.6(3)	C(12)–N(1)–C(1)–C(2)	−1.5(6)
O(43)–S(42)–N(4)–C(4)	−137.2(3)	S(41)–N(4)–C(4)–C(5)	−85.2(4)
O(44)–S(42)–N(4)–C(4)	−9.3(3)	S(42)–N(4)–C(4)–C(3)	−91.5(4)

Table 2. An analysis of the planarity.[a] Distances of relevant atoms from the mean plane, with esds in parentheses.[b]

Plane	Distance/10^{-3} Å
A	C(1) −7(3); C(2) 8(3); C(3) −2(3); C(4) −5(3); C(5) 6(3); C(6) 0(4); N(1)* −34(3); N(4)* −4(2)
B	N(1), C(11), C(12)
C	N(4), S(41), S(42)
D	C(1), C(11), C(12), N(1)* −8(3)
E	C(4), S(41), S(42), N(4)* 57(2)

[a] Angles between planes/°: AB 2.1(2); AC 91.8(2); BC 89.7(2). [b] Atoms with asterisks were not used to define the plane.

planes of the benzene ring and of the S(41)–N(4)–S(42) moiety is 88.2(1)° (see the analysis of the planarity reported in Table 2). The molecular packing is consistent with van der Waals interactions.

Discussion

Fenton's reagent in DMSO affords methyl radicals and methanesulphinic acid in stoicheiometric quantities[8] [see reactions (1) and (2)]. Our original aim was to use the resulting

$$H_2O_2 + Fe^{II} \longrightarrow {}^{\bullet}OH + Fe^{III} + OH^- \quad (1)$$

$$^{\bullet}OH + CH_3SOCH_3 \longrightarrow CH_3^{\bullet} + CH_3SO_2H \quad (2)$$

methyl radical to prepare *N,O*-dimethylated hydroxylamines *via* the two step process described by reactions (3) and (4). Alkyl radicals add readily to nitrosoarenes. Although no absolute

$$CH_3^{\bullet} + Ar\text{-}NO \longrightarrow Ar\text{-}N(O^{\bullet})CH_3 \quad (3)$$

$$CH_3^{\bullet} + Ar\text{-}N(O^{\bullet})CH_3 \longrightarrow Ar\text{-}N(OCH_3)CH_3 \quad (4)$$

kinetic data are available for these reactions, one may obtain a rough estimate of k_3 from relative data. Studies of the addition of the methyl radical to nitrosobenzene in competition with H-abstraction from 2-methylheptane has led to a k_{add}/k_{abs} value of 2.9×10^4.[9] From the value of the rate constant for H-abstraction by methyl radical from 2,2,4-trimethylheptane (20 dm^3 mol^{-1} s^{-1}, ref. 10) one may estimate k_3 to be *ca.* 10^5–10^6 dm^3 mol^{-1} s^{-1}. On the other hand, the coupling of alkyls with aminoxyl radicals is known to be a very fast process, in some cases close to the diffusion-controlled limit.[11] We were therefore surprised to find that the reaction between Fenton's reagent and nitrosoarenes (**1b**), (**1c**), and (**10**) failed to afford any detectable amount of *N,O*-dimethylated hydroxylamines and that the reaction with the unsubstituted nitrosobenzene gave only (**3a**) in 16% yield. The chemistry of alkyl and arylsulphinic acids has been thoroughly investigated.[12] The information available[13,14] indicates that these compounds react spontaneously with nitroso compounds to give the corresponding sulphonylhydroxylamines in high yield [reaction (5)].

$$R\text{-}NO + R'SO_2H \longrightarrow R\text{-}N(OH)SO_2R' \quad (5)$$

Our results indicate that the substituted nitrosoarenes (**1b**) and (**1c**), as well as compound (**10**) react with the sulphinic acid formed in reaction (2) faster than they undergo addition by the methyl radical generated in the same reaction, while with (**1a**) the two processes occur at comparable rates. No detailed mechanistic studies have been carried out on the reactions between nitrosoarenes and sulphinic acids, but it seems con-

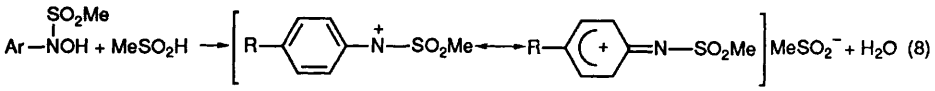
ceivable that they proceed through protonation of the nitroso group followed by nucleophilic attack at the nitrogen by the sulphinate anion [reactions (6) and (7)]. If this is the case, the

$$\text{Ar-NO} + \text{RSO}_2\text{H} \longrightarrow \text{Ar-N}^+\text{OH} + \text{RSO}_2^- \quad (6)$$

$$\text{Ar-N}^+\text{OH} + \text{RSO}_2^- \longrightarrow \text{Ar-N(OH)SO}_2\text{R} \quad (7)$$

electron withdrawing substituents, such as the cyano and protonated dimethylamino groups, should favour their reaction by enhancing the positive charge on the nitrogen atom. This would then explain why in the reactions with (**1b**) and (**1c**) the *N*,*O*-dimethylated hydroxylamines (**3**) were not formed. A similar explanation may be invoked in the case of (**10**), which has an electron withdrawing acetyl group conjugated to the nitroso function. In the absence of an electron withdrawing substituent the addition of methyl radical competes effectively with sulphinic acid and comparable amounts of dimethylated hydroxylamine and sulphonylhydroxylamines are recovered.

The formation of polysulphonated products may be accounted for by a further reaction between the first-formed sulphonylhydroxylamine (**4**) with another molecule of sulphinic acid *via* the intermediacy of a nitrenium ion, reaction (8), in



which the positive charge delocalized on the aromatic ring could explain the $MeSO_2^-$ anion nuclear attack. Although this would fit the formation of (**6c**), (**8c**), (**9c**), or (**12**), the recovery of (**7**) (sulphonylation at a non-conjugated position) and the methyl substitution in (**8c**) seem harder to explain.

The formation of the azoxybenzenes (**2a–c**), most likely formed by reaction of the nitrosoarenes with the corresponding hydroxylamines, is to be attributed to the reducing power of the sulphinic acid;[15] consistently, azoxybenzenes are also obtained by reaction of nitroso compounds with triethylphosphite[16] or ethoxylate[17] whose reducing power is comparable to that of the sulphinate anion $MeSO_2^-$.

The final point which deserves comment is the very low quantity of recovered products (*ca.* 40% overall yield). In recent studies, Asmus[18] and Eberhardt[19] have shown that in the reaction of Fenton's reagent with DMSO, some of the methyl radicals are lost as methane following their reaction with DMSO [reaction (9)]. Although the rate constant for such

$$\text{Me}^\bullet + \text{MeSOMe} \longrightarrow \text{CH}_4 + \text{MeSOCH}_2^\bullet \quad (9)$$

H-abstraction must be very low in comparison with the addition rate constant k_3, we must not forget that DMSO is the reaction medium, and is therefore present in large excess. It has also been pointed out previously[19] that when excess of H_2O_2 over Fe^{II} is used, methyl radicals may be intercepted by hydrogen peroxide to give methane once again [reaction (10)].

$$\text{Me}^\bullet + \text{H}_2\text{O}_2 \longrightarrow \text{CH}_4 + {}^\bullet\text{OOH} \quad (10)$$

We believe that reactions (9) and (10) combined together may explain the low overall yields obtained.

Experimental

M.p.s were determined on an Electrothermal apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian XL 100 (FT mode) spectrometer using TMS as internal standard; chemical shifts are in ppm. Preparative-layer chromatography (PLC) was carried out on 0.1 × 20 × 20 cm plates of silica gel Merck 60 PF_{254}. ESR spectra were obtained on a Varian E4 instrument in $CHCl_3$ solution. Compound (**1a**) was a Merck-Schuchardt commercial product. Compounds (**1b**), (**1c**), and (**10**) were prepared according to the literature methods.[20–22] Samples for comparison with (**2a–c**) were prepared as described in the literature.[23,24]

Reaction of Nitrosoarenes (**1a–c**) *and* (**10**) *with Fenton's Reagent in DMSO. General Procedure.*—Hydrogen peroxide (6 mmol; 40% aq.) in DMSO (2 cm^3) was added to nitrosoarene (2 mmol) and $FeSO_4 \cdot 7H_2O$ (0.4 mmol) in DMSO (3 cm^3), dropwise with stirring over 15 min, keeping the temperature under 25 °C. After 45 min at room temperature the reaction mixture was poured into water and extracted with chloroform (3 × 10 cm^3). The organic layer was washed with water (2 × 10 cm^3), separated, and dried over Na_2SO_4. The solution was evaporated to dryness to give a residue which, when taken up in benzene (5 cm^3), was chromatographed on a column (SiO_2), using cyclohexane–ethyl acetate and benzene–acetone mixtures as eluants (ratio specified in each case). The isolated fractions were further purified by PLC.

Reaction with Nitrosobenzene (**1a**).—Starting from (**1a**) (1 070 mg; 10 mmol) and using cyclohexane–ethyl acetate (9:1) as eluant the following compounds were obtained: azoxybenzene (**2a**), 130 mg (13%), identified by comparison with an authentic sample; *N*-methyl-*N*-methoxyaniline (**3a**), 220 mg (16%), m.p. 53–55 °C from ligroin (80–100 °C); $\delta_H(CDCl_3)$ 2.81 (3 H, s, NMe), 3.88 (3 H, s, NOMe), and 7.38 (5 H, m, Ar); *m/z* 137 (M^+, 0.8%), 122 (100), 107 (40), and 77 (31) (Found: C, 69.8; H, 8.1; N, 10.1%, M^+, 137. Calc. for $C_8H_{11}NO$: C, 70.03; H, 8.08; N, 10.21; *M*, 137.2); *N*-methanesulphonylhydroxylamine (**4a**): 200 mg (11%), m.p. 110–112 °C from benzene–ligroin (80–100 °C); ν_{max}(Nujol) 3 320 (N–OH), 1 600, and 1 150 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 2.86 (3 H, s, SO_2Me), and 7.64–7.36 (6 H, m, Ar + NOH); *m/z* 187 (M^+, 8.9), 171 (4.1), 108 (79.0), and 78 (100) (Found: C, 44.7; H, 4.8; N, 7.4; S, 17.2; M^+, 187. Calc. for $C_7H_9NSO_3$: C, 44.91; H, 4.85; N, 7.48; S, 17.13; M^+, 187.2).

Reaction with 4-*Cyanonitrosobenzene* (**1b**).—Starting from (**1b**) (3 mmol, 396 mg) and using cyclohexane–ethyl acetate (8:2) as eluant the following compounds were isolated: 4,4′-dicyanoazoxybenzene (**2b**) 50 mg (13%), identified by comparison with an authentic sample; 4-cyano-*N*-methanesulphonylhydroxylamine (**4b**) 200 mg (31%), m.p. 160–162 °C from benzene; ν_{max}(Nujol) 3 315 (N–OH), 2 247 (CN), 1 610, and 1 170 cm^{-1} (SO_2Me); $\delta_H([^2H_6]DMSO)$ 2.96 (3 H, s, SO_2Me), 7.8 (4 H, pseudo-q, A_2B_2, Ar), and 11.30 (1 H, s, NOH); *m/z* 212 (M^+, 8.7%), 196 (2.7), 132 (100), and 102 (93.5) (Found: C, 45.4; H, 3.9; N, 13.1; S, 14.9; M^+, 212. Calc. for $C_8H_8N_2SO_3$: C, 45.98; H, 3.8; N, 13.20; S, 15.11; M^+, 212.2).

Reaction with p-*Nitroso*-N,N-*dimethylaniline* (**1c**).—Starting from (**1c**) (1 500 mg, 10 mmol) and using benzene–acetone (9:1) as eluant the following were isolated: 4,4′-dimethylazoxybenzene (**2c**) 160 mg (11%), identified by comparison with an authentic sample; *p*-nitro-*N*,*N*-dimethylaniline (**5c**) 160 mg (9.6%), identified by comparison with an authentic sample (prepared by a separate method described later); 2-methanesulphonyl-4-(*N*,*N*-dimethylamino)-*N*-methanesulphonanilide (**6c**) 270 mg (9.2%), m.p. 125–126 °C from ethanol; ν_{max}(Nujol) 3 350 (NH), 1 615, 1 160, and 1 140 cm^{-1} (SO_2Me); $\delta_H(CDCl_3)$ 2.98 (6 H, s,

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for non-H atoms with esds in parentheses.

	x	*y*	*z*
S(41)	8 649(1)	1 172(1)	5 261(1)
S(42)	8 409(0)	4 827(1)	4 497(1)
O(41)	9 489(2)	1 781(4)	5 720(3)
O(42)	8 274(2)	60(3)	6 013(3)
O(43)	8 965(2)	4 377(4)	3 719(3)
O(44)	7 689(2)	5 879(3)	3 998(3)
N(1)	4 586(2)	2 444(4)	5 044(3)
N(4)	8 033(2)	2 948(3)	4 969(2)
C(1)	5 424(2)	2 583(4)	5 000(3)
C(2)	6 029(2)	3 161(4)	6 050(3)
C(3)	6 874(2)	3 261(4)	6 033(3)
C(4)	7 142(2)	2 825(4)	4 983(3)
C(5)	6 567(2)	2 289(4)	3 938(3)
C(6)	5 710(2)	2 164(5)	3 954(3)
C(11)	3 952(3)	1 924(7)	3 952(5)
C(12)	4 303(3)	2 830(7)	6 139(4)
C(41)	8 562(3)	159(6)	3 818(4)
C(42)	8 990(3)	5 786(6)	5 853(4)

NMe_2), 3.12 (3 H, s, OSO_2Me), 3.14 (3 H, s, SO_2Me), 6.9 (1 H, pseudo-q, Ar, *J* 8.2, 2.1 Hz), and 8.12 (1 H, broad, NH); *m/z* 292 (M^+, 26%), 227 (7), 213 (100), 149 (70), 133 (18), and 122 (15) (Found: C, 40.8; H, 5.6; N, 9.5; S, 21.8; M^+, 292. Calc. for $C_{10}H_{16}N_2O_4S_2$: C, 41.07; H, 5.52; N, 9.58; S, 21.94; M^+, 292.4); 3-methanesulphonyl-4-*N*,*N*-dimethylamino-*N*-methanesulphonanilide (**7c**) 210 mg (7.2%), m.p. 163–165 °C from ethanol; ν_{max}(Nujol) 3 200 (NH), 1 150, 1 145, and 1 130 cm^{-1} (SO_2Me); $\delta_H(CDCl_3)$ 2.63 (6 H, s, NMe_2), 2.86 (3 H, s, SO_2Me), 3.20 (3 H, s, NSO_2Me), 7.27 (1 H, d, arom, *J* 8.4 Hz), 7.51 (1 H, pseudo-q, arom, *J* 8.4, 2.2 Hz), 7.77 (1 H, d, Ar, *J* 2.2 Hz), and 9.4 (1 H, broad, NH); *m/z* 292 (M^+, 38%), 213 (100), 170 (10), 165 (12), 134 (88), 133 (89), 120 (25), and 119 (100) (Found: C, 40.7; H, 5.3; N, 9.6; S, 21.7; M^+, 292. Calc. for $C_{10}H_{16}N_2O_4S_2$: C, 41.07; H, 5.52; N, 9.58; S, 21.94; M^+, 292.4); 3-methyl-2-methanesulphonyl-4-(*N*,*N*-dimethylamino)-*N*-methanesulphonanilide (**8c**) 120 mg (3.9%); m.p. 148–149 °C from ethanol; ν_{max}(Nujol) 3 320 (NH), and 1 155 cm^{-1} (SO_2Me), $\delta_H(CDCl_3)$ 2.66 (6 H, s, NMe_2), 3.07 (3 H, s, SO_2Me), 3.20 (3 H, s, SO_2Me), 7.4 (2 H, pseudo-q, AB), and 9.4 (1 H, broad, NH); *m/z* 306 (M^+, 30%), 227 (100), 148 (51), 147 (25), 133 (34), 132 (21), 79 (74), and 77 (25) (Found: C, 43.4; H, 5.8; N, 9.0; S, 21.1, M^+, 306. Calc. for $C_{11}H_{18}N_2O_4S_2$: C, 43.12; H, 5.92; N, 9.14; S, 20.93, M^+, 306.4); 4-(*N*,*N*-dimethylamino)-*N*,*N*-dimethanesulphonanilide (**9c**) 125 mg (4.3%), m.p. 220 °C from ethanol; ν_{max}(Nujol) 1 610, 1 535, and 1 165 cm^{-1} (SO_2Me); $\delta_H(CDCl_3)$ 2.86 (6 H, s, NMe_2), 3.24 [6 H, s, $(SO_2Me)_2$], 6.79 (4 H, Ar, A_2B_2); *m/z* 292 (M^+, 11%), 213 (85), 134 (100), and 119 (21) (Found: C, 40.9; H, 5.6; N, 9.4; S, 21.7; M^+, 292. Calc. for $C_{10}H_{16}N_2O_4S_2$: C, 41.07; H, 5.52; N, 9.58; S, 21.94; M^+, 292.4).

Reaction with 1-*Nitroso*-2-*phenyl*-3-*acetylindolizine* (**10**).—Starting from (**10**) (528 mg, 2 mmol) and using benzene–acetone (9:1) as eluant, the following compounds were isolated: 1-(*N*-methanesulphonyl)-2-phenyl-3-acetylindolizine (**11**) 80 mg (12%), m.p. 202 °C from ethanol; ν_{max}(Nujol) 3 100 (NH, broad), 1 590, and 1 155 cm^{-1} (SO_2Me); $\delta_H(CDCl_3)$ 2.0 (3 H, s, COMe), 2.48 (3 H, s, SO_2Me), 6.18 (1 H, broad, NH), 6.96 (1 H, pseudo-t, Ar), 7.20–7.58 (6 H, m, Ar), 7.85 (1 H, d, Ar), and 9.64 (1 H, d, Ar); *m/z* 328 (M^+, 6.4%), 263 (8.8), 249 (M^+ – SO_2Me, 100), 206 (56.3), 129 (17.5), 79 (36.9), and 78 (36.8) (Found: C, 62.2; H, 4.7; N, 8.4; S, 9.9%; M^+, 328. Calc. for $C_{17}H_{16}N_2O_3S$: C, 62.2; H, 4.91; N, 8.53; S, 9.77; M^+, 328.4); 1-*N*,*N*-dimethanesulphonyl)-2-phenyl-3-acetylindolizine (**12**) 60 mg (7.4%), m.p. 250 °C from ethyl acetate; ν_{max}(Nujol) 1 640, 1 160, and 1 165 cm^{-1} (SO_2Me); $\delta_H(CDCl_3)$ 1.99 (3 H, s, COMe), 3.10 (6 H, s, SO_2Me), 7.00 (1 H, pseudo-t, Ar), 7.33–7.63 (7 H, m, Ar), and 9.56 (1 H, d, Ar); *m/z* 406 (M^+, 1.9%), 328 (9.1), 327 (M^+ – SO_2Me, 45.1), 248 [M^+ – $(SO_2Me)_2$, 18.0], 205 (23.0), 129 (100), and 79 (39.7) (Found: C, 53.1; H, 4.6; N, 6.8; S, 15.5; M^+, 406. Calc. for $C_{18}H_{18}N_2O_5S_2$: C, 53.18; H, 4.46; N, 6.89; S, 15.78; M^+, 406.5).

Reaction of Methanesulphinic Acid with Nitrosobenzene.—Hydrogen peroxide (40% aq., 576 mg, 6 mmol) in DMSO (2 cm^3) was added dropwise to a solution of $FeSO_4 \cdot 7H_2O$ (111 mg, 0.4 mmol) with stirring, keeping the temperature < 25 °C. After 40 min at room temperature, nitrosobenzene (214 mg, 2 mmol in 3 cm^3 of DMSO) was added to the mixture. After 30 min the reaction was poured into water (20 cm^3) and extracted with chloroform (3 × 10 cm^3). The organic layer was separated, dried, and evaporated to dryness. The residue, taken up in benzene (5 cm^3), was chromatographed on an SiO_2 column, eluting with cyclohexane–ethyl acetate (9:1); to yield compound (**4a**) (57 mg).

4-*Nitro*-N,N-*dimethylaniline* (**5c**).—*m*-Chloroperbenzoic acid (200 mg, 1.16 mmol) was added over 15 min to a solution of 4-nitroso-*N*,*N*-dimethylaniline (150 mg, 1 mmol in 15 cm^3 of $CHCl_3$) with stirring at room temperature. After 30 min the reaction mixture was extracted with aq. NaOH (10%; 10 cm^3). The chloroform layer was then separated, dried (Na_2SO_4) and evaporated to dryness. The yellow residue recrystallization from EtOH gave 110 mg of the nitro-derivative, m.p. 160–162 °C (lit.,[25] 162–165 °C).

Nitroxides (**13a**) *and* (**13b**).—Hydroxylamine (**4a**) (2 cm^3 of a 10^{-2} mol dm^{-3} $CHCl_3$ solution and PbO_2 (3 mg) were each placed into one of the two legs of an inverted U-cell[26] and the cell was degassed with pure nitrogen. The solution was shaken with PbO_2 and poured into the ESR aqueous cell. The ESR signal of (**13a**) was recorded. Nitroxide (**13b**) was prepared in the same way starting from (**4b**). The *g*-factor values were determined by simultaneous comparison with diphenylpicrylhydrazyl.

Crystal Structure of 4-N,N-*Dimethylamino*-N,N-*di*(*methanesulphonyl*)*aniline*.—Crystals were tabular pale yellow prisms. Lattice constants were determined by using a program[27] which repeatedly rectifies on the diffractometer the values of (θ,χ,φ) angles of thirty reflections ($20 \leqslant \theta \leqslant 30°$) to obtain the maximum of the peak when the angles do not vary within 0.01°.

Crystal data. $C_{10}H_{16}N_2O_4S_2$, M = 292.4. Monoclinic, a = 16.232(4), b = 7.623(2), c = 11.110(3) Å; β = 103.2(1)°; V = 1 338.4(8) Å^3; Z = 4; D_c = 1.45 g cm^{-3}; Cu-K_α radiation, λ = 1.5418 Å; μ(Cu-K_α) = 36.5 cm^{-1}. Space group $P2_1/n$ (C_{2h},[5] N° 14) from systematic absences. X-Ray measurements were performed at T = 293 K on a Siemens AED single-crystal diffractometer on line to an IBM PS/2 M30 computer, in the range ($3 < \theta < 70°$) using Cu-K_α radiation. The diffraction angle θ for every reflection was determined on the basis of the orientation matrix and the outline of the diffraction peak was collected in θ–2θ step scanning mode using a scan width from (θ–0.60)° to (θ + 0.60 + $\Delta\lambda/\lambda tg\theta$)°. The intensities I_{hkl} were determined by analysing the reflection profile using the Lehmann and Larsen procedure.[28] 2 537 symmetry independent reflections ($-19 \leqslant h \leqslant 19$, $0 \leqslant k \leqslant 9$, $0 \leqslant l \leqslant 13$) were measured, of which 1 658 (internal R merging factor 0.035) with $I_{hkl} > 2\sigma(I_{hkl})$ [$\sigma(I)$ based on statistic counting] were used in the refinement. One 'standard' reflection, measured every 50 collected reflections to monitor crystal decomposition and instrumental linearity, showed no significant variation. The specimen was a fragment of crystal of dimensions

(0.19 × 0.08 × 0.48 mm. Corrections for Lorentz and polarization effects were applied, with no corrections for absorption effect.

Structure analysis and refinement. The structure was solved by SHELX86[29] and refined by SHELX76[29] with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.049$, $R_w = 0.048$; $\Sigma w(F_o - F_c)^2$ minimized with $w = [\sigma^2(F_o) + 0.014\ F_o^2]^{-1}$. All the hydrogen atoms were located in the ΔF map. Positional parameters are given in Table 3. Atomic scattering factors were from ref. 30 for non-hydrogen atoms and from ref. 31 for hydrogen. Tables of thermal parameters and hydrogen atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre.*

The calculations were carried out on the GOULD 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR of Parma, Italy. Bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy.

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* For details of the CCDC deposition scheme see 'Instructions for Authors' (1990), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

References

1 C. Giordano, F. Mimisci, V. Tortelli, and E. Vismara, *J. Chem. Soc., Perkin Trans. 2*, 1984, 293.
2 F. Minisci, *Synthesis*, 1973, 1; F. Minisci, *Top Curr. Chem.*, 1976, **62**, 1.
3 M. J. Perkins, in 'Advances in Physical Organic Chemistry,' eds. V. Gold and D. Bethell, Academic Press, New York, 1980, vol. 1, p. 178; G. Gronki, P. Courbis, P. Tordo, G. Mousset, and J. Simonet, *J. Phys. Chem.*, 1983, **87**, 1343.
4 A. L. J. Beckwith, V. W. Bowry, M. O'Leary, G. Moad, E. Rizzardo, and D. H. Solomon, *J. Chem. Soc., Chem. Commun.*, 1986, 1003.
5 E. G. Rozantsev and V. Sholle, *Synthesis*, 1971, 190; L. Greci, *Tetrahedron*, 1982, **38**, 2435.
6 D. Mulvey and W. A. Waters, *J. Chem. Soc., Perkin Trans. 2*, 1974, 666.
7 C. Rizzoli, P. Sgarabotto, F. Ugozzoli, L. Cardellini, L. Greci, and P. Stipa, *Acta Crystallogr.*, submitted for publication.
8 U. Rudqvist and K. Torsell, *Acta Chem. Scand.*, 1971, **25**, 2183.
9 W. J. Heliman, A. Rembaum, and M. Swarz, *J. Chem. Soc., Chem. Commun.*, 1957, 1127.
10 R. H. Schuler and R. R. Kuntz, *J. Phys. Chem.*, 1963, **67**, 1004.
11 P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, 1978, **100**, 2493; T. Doba, S. Nodo, and H. Yoshida, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 21; A. L. J. Beckwith, V. W. Bowry, and G. Moad, *J. Org. Chem.*, 1988, **53**, 1632.
12 S. Oae and N. Kunieda in 'Organic Chemistry of Sulfur,' ed. S. Oae, Plenum Press, New York, London, 1977, p. 603.
13 A. J. W. Wayer, H. W. Geluk, J. B. F. N. Engberts, and Th. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 696.
14 E. Yu. Belyaev, L. M. Gornostaev, and G. A. Suboch, *Khim. Teknol. Polim.*, 1975, **4**, 60 (Russian); (*Chem. Abstr.*, 1977, **86**, 189390s).
15 S. Oae and N. Kunieda in 'Organic Chemistry of Sulfur,' ed. S. Oae, Plenum Press, New York, London, 1977, p. 613.
16 P. J. Bunyan and J. I. Cagodan, *J. Chem. Soc.*, 1963, 42.
17 A. Osuka, H. Shimizu, and H. Suzuki, *Chem. Lett.*, 1983, 1373.
18 D. Veltwisch, E. Janata, and K. D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1980, 146.
19 M. K. Eberhardt, R. Colina, *J. Org. Chem.*, 1988, **53**, 1071.
20 J. H. Ashley and S. S. Berg, *J. Chem. Soc.*, 1957, 3889.
21 A. I. Vogel, in 'Practical Organic Chemistry,' Longmans, London, 1964, p. 573.
22 J. M. Tedder and K. H. Todd, *J. Chem. Soc. C*, 1969, 1279.
23 A. I. Vogel, in 'Practical Organic Chemistry,' Longmans, London, 1964, p.630.
24 J. Hutton and A. Waters, *J. Chem. Soc. B*, 1968, 191.
25 J. B. Tingle, F. C. Blanck, *J. Am. Chem. Soc.*, 1908, **30**, 1395.
26 J. A. Russell, E. G. Janzen, and T. Storm, *J. Am. Chem. Soc.*, 1964, **86**, 1807.
27 D. Belletti, F. Ugozzoli, A. Cantoni, and G. Pasquinelli, 'Gestione on line di Diffrattometro a cristallo singolo Siemens AED con sistema General Authomation Jumbo 220,' Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy, 1979. Int. Rep. 1–3/79.
28 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
29 G. M. Sheldrick, SHELX76, SHELX86. Computer Programs for Crystal Structure Determination, 1976 and 1986, University of Cambridge, UK.
30 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
31 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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