

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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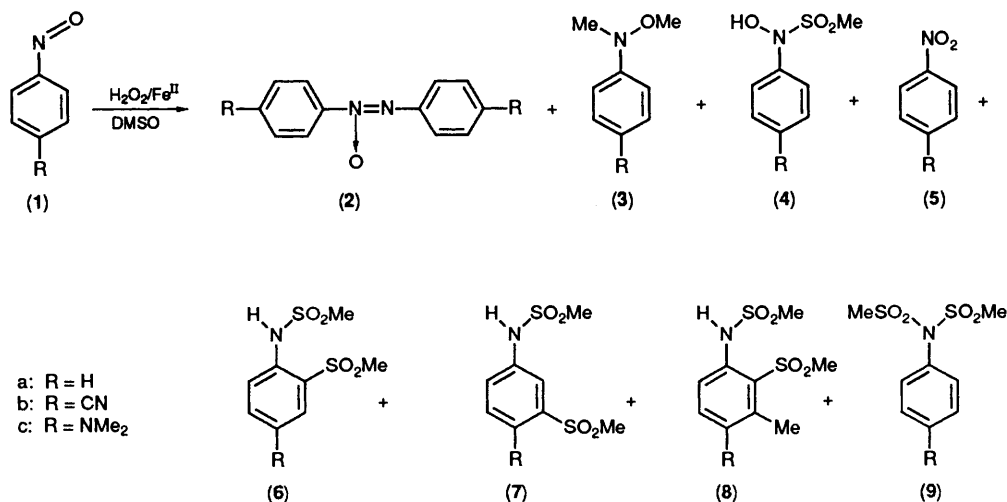
On treatment with Fenton's reagent in dimethyl sulphoxide nitrosoarenes form sulphonylate products, while the expected *N,O*-dimethylated hydroxylamine is isolated only in the case of nitrosobenzene in low yield. Nitrosobenzene and 4-cyanonitrosobenzene lead to *N*-sulphonylhydroxylamines while 4-nitroso-*N,N*-dimethylaniline and 1-nitroso-2-phenyl-3-acetylidolizine 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 $\text{H}_2\text{O}_2/\text{Fe}^{\text{II}}$ 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-acetylidolizine (**10**) with $\text{H}_2\text{O}_2/\text{Fe}^{\text{II}}$ 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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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 3340 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



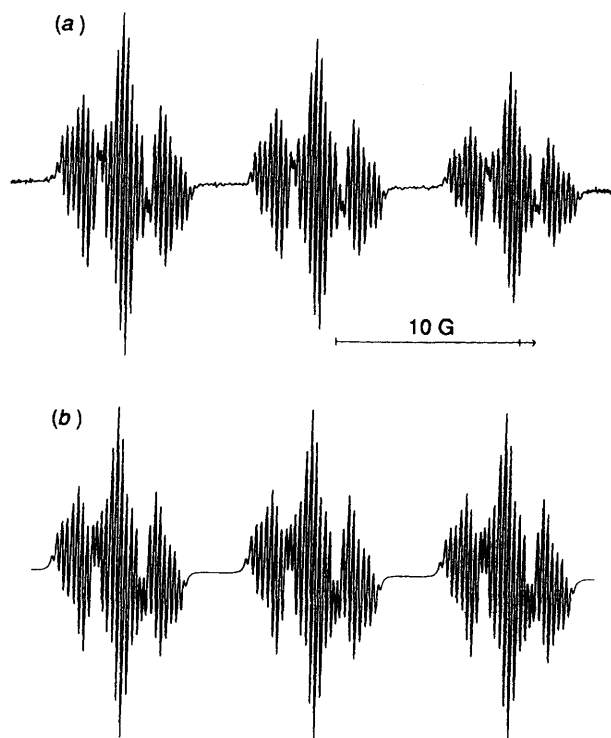
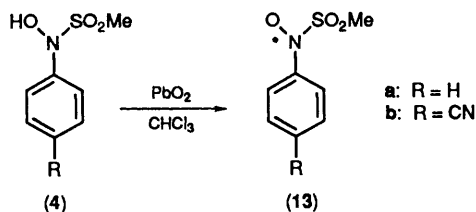


Figure 1. ESR spectrum of (13a) recorded at room temperature: (a) experimental; (b) computer simulated with a line width of 0.15 G.

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 SO₂Me and *pseudo*-quartet at δ 7.80 for the A₂B₂ aromatic protons). Again, treatment of (4a) with PbO₂ 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 A₂B₂ system centred at δ 6.79 due to the four aromatic protons; owing to the uncertainty about the molecular ion

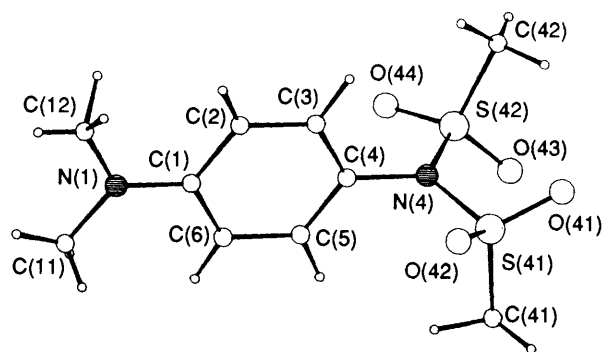
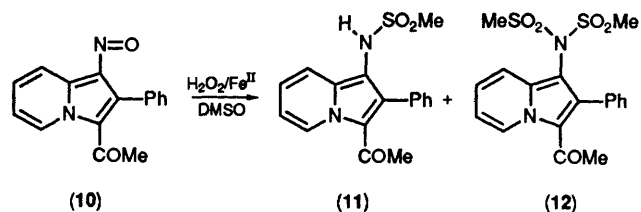


Figure 2. Perspective view of 4-*N,N*-dimethylamino-*N,N*-dimethanesulphonyl aniline (9c).

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 $M - \text{SO}_2\text{Me}$, while compound (12) shows two main peaks at mass $M - \text{SO}_2\text{Me}$ and $M - 2\text{SO}_2\text{Me}$, as expected from the structures proposed. For compound (11) the NMR signals of COMe and SO₂Me 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 SO₂Me).

Compounds (4b), (6c)–(9c), (11) and (12) all exhibited in their IR spectra an absorption at *ca.* 1 150 cm⁻¹, typical of the SO₂Me 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 pyramidal nature 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.

<i>Bond distances</i>			
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)
<i>Bond angles</i>			
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)
<i>Torsion angles</i>			
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

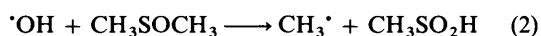
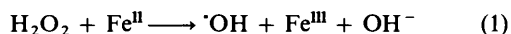
Plane	Distance/10 ^{–3} Å
A	C(1) –7(3); C(2) 8(3); C(3) –2(3); C(4) –5(3); C(5) 6(3); C(6) 0(4); N(1)* –34(3); N(4)* –4(2)
B	N(1), C(11), C(12)
C	N(4), S(41), S(42)
D	C(1), C(11), C(12), N(1)* –8(3)
E	C(4), S(41), S(42), N(4)* 57(2)

^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.

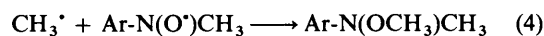
planes of the benzene ring and of the S(41)–N(4)–S(42) moiety is 88.2(1)° (see the analysis of the planarity reported in Table 2). The molecular packing is consistent with van der Waals interactions.

Discussion

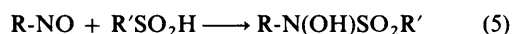
Fenton's reagent in DMSO affords methyl radicals and methanesulphonic acid in stoichiometric quantities⁸ [see reactions (1) and (2)]. Our original aim was to use the resulting



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

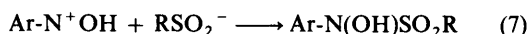
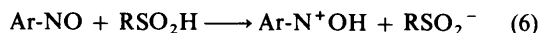


kinetic data are available for these reactions, one may obtain a rough estimate of k_3 from relative data. Studies of the addition of the methyl radical to nitrosobenzene in competition with H-abstraction from 2-methylheptane has led to a $k_{\text{add}}/k_{\text{abs}}$ value of 2.9×10^4 .⁹ From the value of the rate constant for H-abstraction by methyl radical from 2,2,4-trimethylheptane ($20 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, ref. 10) one may estimate k_3 to be $ca. 10^5\text{--}10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. 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 arylsulphonic 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)].



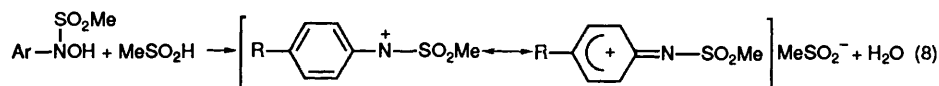
Our results indicate that the substituted nitrosoarenes (**1b**) and (**1c**), as well as compound (**10**) react with the sulphonic acid formed in reaction (2) faster than they undergo addition by the methyl radical generated in the same reaction, while with (**1a**) the two processes occur at comparable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



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



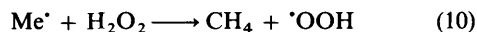
which the positive charge delocalized on the aromatic ring could explain the MeSO_2^- anion nuclear attack. Although this would fit the formation of (6c), (8c), (9c), or (12), the recovery of (7) (sulphonylation at a non-conjugated position) and the methyl substitution in (8c) seem harder to explain.

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 triethylphosphite¹⁶ or ethoxylate¹⁷ 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, Asmus¹⁸ and Eberhardt¹⁹ 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



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 previously¹⁹ 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)].



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. ¹H NMR spectra were recorded on a Varian XL 100 (FT mode) spectrometer using TMS as in-

ternal 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 PF₂₅₄. 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 cm³) was added to nitrosoarene (2 mmol) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.4 mmol) in DMSO (3 cm³), 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 cm³). The organic layer was washed with water (2 × 10 cm³), separated, and dried over Na_2SO_4 . The solution was evaporated to dryness to give a residue which, when taken up in benzene (5 cm³), 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); $\delta_{\text{H}}(\text{CDCl}_3)$ 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 $\text{C}_8\text{H}_{11}\text{NO}$: 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); $\nu_{\text{max}}(\text{Nujol})$ 3 320 (N–OH), 1 600, and 1 150 cm⁻¹ (SO_2); $\delta_{\text{H}}(\text{CDCl}_3)$ 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 $\text{C}_7\text{H}_9\text{NSO}_3$: 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; $\nu_{\text{max}}(\text{Nujol})$ 3 315 (N–OH), 2 247 (CN), 1 610, and 1 170 cm⁻¹ (SO_2Me); $\delta_{\text{H}}([\text{}^2\text{H}_6]\text{DMSO})$ 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 $\text{C}_8\text{H}_8\text{N}_2\text{SO}_3$: 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; $\nu_{\text{max}}(\text{Nujol})$ 3 350 (NH), 1 615, 1 160, and 1 140 cm⁻¹ (SO_2Me); $\delta_{\text{H}}(\text{CDCl}_3)$ 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)

NMe₂), 3.12 (3 H, s, OSO₂Me), 3.14 (3 H, s, SO₂Me), 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 C₁₀H₁₆N₂O₄S₂: C, 41.07; H, 5.52; N, 9.58; S, 21.94; *M*⁺, 292.4); 3-methanesulphonyl-4-*N,N*-dimethylamino-*N*-methanesulphonanilide (**7e**) 210 mg (7.2%), m.p. 163–165 °C from ethanol; *v*_{max}(Nujol) 3 200 (NH), 1 150, 1 145, and 1 130 cm⁻¹ (SO₂Me); δ_H(CDCl₃) 2.63 (6 H, s, NMe₂), 2.86 (3 H, s, SO₂Me), 3.20 (3 H, s, NSO₂Me), 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 C₁₀H₁₆N₂O₄S₂: 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; *v*_{max}(Nujol) 3 320 (NH), and 1 155 cm⁻¹ (SO₂Me), δ_H(CDCl₃) 2.66 (6 H, s, NMe₂), 3.07 (3 H, s, SO₂Me), 3.20 (3 H, s, SO₂Me), 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 C₁₁H₁₈N₂O₄S₂: 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; *v*_{max}(Nujol) 1 610, 1 535, and 1 165 cm⁻¹ (SO₂Me); δ_H(CDCl₃) 2.86 (6 H, s, NMe₂), 3.24 [6 H, s, (SO₂Me)₂], 6.79 (4 H, Ar, A₂B₂); *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 C₁₀H₁₆N₂O₄S₂: 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; *v*_{max}(Nujol) 3 100 (NH, broad), 1 590, and 1 155 cm⁻¹ (SO₂Me); δ_H(CDCl₃) 2.0 (3 H, s, COMe), 2.48 (3 H, s, SO₂Me), 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*⁺ – SO₂Me, 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 C₁₇H₁₆N₂O₃S: 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; *v*_{max}(Nujol) 1 640,

1 160, and 1 165 cm⁻¹ (SO₂Me); δ_H(CDCl₃) 1.99 (3 H, s, COMe), 3.10 (6 H, s, SO₂Me), 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*⁺ – SO₂Me, 45.1), 248 [*M*⁺ – (SO₂Me)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 C₁₈H₁₈N₂O₅S₂: 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 cm³) was added dropwise to a solution of FeSO₄·7H₂O (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 cm³ of DMSO) was added to the mixture. After 30 min the reaction was poured into water (20 cm³) and extracted with chloroform (3 × 10 cm³). The organic layer was separated, dried, and evaporated to dryness. The residue, taken up in benzene (5 cm³), was chromatographed on an SiO₂ 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 cm³ of CHCl₃) with stirring at room temperature. After 30 min the reaction mixture was extracted with aq. NaOH (10%; 10 cm³). The chloroform layer was then separated, dried (Na₂SO₄) 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 cm³ of a 10⁻² mol dm⁻³ CHCl₃ solution and PbO₂ (3 mg) were each placed into one of the two legs of an inverted U-cell²⁶ and the cell was degassed with pure nitrogen. The solution was shaken with PbO₂ 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 program²⁷ which repeatedly rectifies on the diffractometer the values of (θ, χ, φ) angles of thirty reflections (20 ≤ θ ≤ 30°) to obtain the maximum of the peak when the angles do not vary within 0.01°.

Crystal data. C₁₀H₁₆N₂O₄S₂, *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) Å³; *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 *P*2₁/*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 < θ < 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+Δλ/λtgθ)°. The intensities *I*_{hkl} were determined by analysing the reflection profile using the Lehmann and Larsen procedure.²⁸ 2 537 symmetry independent reflections (–19 ≤ *h* ≤ 19, 0 ≤ *k* ≤ 9, 0 ≤ *l* ≤ 13) were measured, of which 1 658 (internal *R* merging factor 0.035) with *I*_{hkl} > 2σ(*I*_{hkl}) [σ(*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 SHELX86²⁹ and refined by SHELX76²⁹ with cycles of full-matrix anisotropic least-squares (hydrogen atoms isotropically) up to $R = 0.049$, $R_w = 0.048$; $\sum w(F_o - F_c)^2$ 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.

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