Sulphur–Nitrogen Compounds. Part 5.[1] The Oxidation of *N*-Aryl-*N*-(arylsulphonyl)hydroxylamines: Preparation of *N*-Aryl-*NO*-bis(arylsulphonyl)hydroxylamines

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Oxidation of the compounds $R^1(R^2SO_2)NOH$ (R^1, R^2 = Ph, Ph; p-ClC_6H_4, Ph; p-ClC_6H_4, p-$MeOC_6H_4$; or Ph, Me) yields *NNO*-trisubstituted hydroxylamines $R^1(R^2SO_2)NOSO_2R^2$, together with R^1NO_2 and $R^1NN(O)R^1$. When R^1, R^2 = Ph, Ph; p-ClC_6H_4, Ph; or Ph, Me the oxidation proceeds *via* rhe aminyl oxide radicals $R^1(R^2SO_2)NO^{\cdot}$: when R^1, R^2 = p-ClC_6H_4, p-$MeOC_6H_4$ the radical $(p\text{-}ClC_6H_4)_2NO^{\cdot}$ is also formed. Apparently pure samples of $(RSO_2)_2NOSO_2R$ (R = p-XC_6H_4; X = H, Me, Cl, or F) contain low concentrations of the radicals $(RSO_2)_2NO^{\cdot}$. Carbon-13 n.m.r. spectroscopy shows that the compounds $(RSO_2)_2NH$, $(RSO_2)_2NOH$, and $(RSO_2)_3N$ contain only one type of R, but that $(RSO_2)_2NOSO_2R$ contain two types of R and hence are *NNO*-trisubstituted hydroxylamines rather than amine oxides. Similarly $Ph(PhSO_2)NOH$ contains two phenyl sites but $Ph(PhSO_2)NOSO_2Ph$ contains three.

OXIDATION of diarylhydroxylamines leads [2] to diarylaminyl oxides R_2NO whereas oxidation of bis(arylsulphonyl)hydroxylamines leads [3] to tris(arylsulphonyl)hydroxylamines, $(RSO_2)_2NOSO_2R$. Accordingly, we have investigated the oxidation of some mixed hydroxylamines $R^1(R^2SO_2)NOH$, and report here the results of this work, together with those of a ^{13}C n.m.r. study of some arylsulphonylhydroxylamines and related species.

EXPERIMENTAL

Literature methods were used for the preparation of the compounds p-$XC_6H_4SO_2Na$ (X = H, Me, Cl, F, or OMe),[3] $(p\text{-}XC_6H_4SO_2)_2NOH$,[3] $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$,[3] $(p\text{-}MeC_6H_4SO_2)_3N$,[4] $Ph(PhSO_2)NOH$,[5] and $Ph(PhCO)NOH$.[6] The compounds $R^1(R^2SO_2)NOH$ were prepared by reaction [5] of R^1NHOH with R^2SO_2Cl: microanalytical data, yields, and melting points are in Table 1.

E.s.r. spectra were recorded using a Decca X-3 instrument, ^{13}C n.m.r. spectra on a Varian CFT-20 spectrometer.

Oxidation of N-*Aryl*-N-*arylsulphonylhydroxylamines*.—(*a*) $Ph(PhSO_2)NOH$. The hydroxylamine (2.49 g, 10.0 mmol) was stirred during 24 h with an excess of PbO_2 in benzene (100 cm^3); the mixture was then centrifuged, and the solution reduced to small volume. Light petroleum (200 cm^3) was added and the mixture vigorously shaken; the petroleum layer was carefully decanted off, and filtered to yield the crude *N*-phenyl-*NO*-bis(phenylsulphonyl)hydroxylamine which was recrystallised from benzene (0.80 g, 2.1 mmol, 42%), m.p. 110—112 °C (Found: C, 55.9; H, 4.2; N, 3.6. Calc. for $C_{18}H_{15}NO_5S_2$: C, 55.5; H, 3.9; N, 3.6%). Extrac-

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[1] Part 4, J. D. Birchall and C. Glidewell, *Inorg. Chim. Acta*, 1977, **25**, L67.

[2] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, New York, 1968.

[3] J. D. Birchall and C. Glidewell, *J.C.S. Dalton*, 1977, 10.

[4] H. Stetter and H. Hansmann, *Ber.*, 1957, **90**, 2728.

[5] T. A. J. W. Wajer, H. W. Geluk, J. B. F. N. Engberts, and T. J. de Boer, *Rec. Trav. chim.*, 1970, **89**, 696.

[6] E. Bamberger, K. Blaskopf, and A. Landau, *Ber.*, 1919, **52**, 1116.

tion of the residual oil with hot ethanol afforded azoxybenzene (0.10 g, 0.52 mmol, 10.4%), m.p. 33—34 °C (lit.,[7] 36 °C). Nitrobenzene was detected mass spectrometrically. Identical products were obtained when the oxidant was $Pb[O_2CMe]_4$ in CH_2Cl_2, but the following reagents failed to oxidise the hydroxylamine: AgO–C_6H_6, MnO_2–C_6H_6, and HNO_3–$MeCO_2H$. With aqueous HNO_2 as oxidant, the sole product (60%) was p-$ONC_6H_4(PhSO_2)NOH$ (Found: C, 52.0; H, 3.5; N, 10.1. Calc. for $C_{12}H_{10}N_2O_4S$: C, 51.8; H, 3.6; N, 10.1%), m.p. 85—86 °C, m/e 278.036 23 u [u = $(10^3 N_A)^{-1}$ kg] ($^{12}C_{12}{}^{1}H_{10}{}^{14}N_2{}^{16}O_4{}^{32}S$ requires 278.036 12 u). Hydrogen n.m.r. spectrum: δ 6.30 and 7.65 (A_2B_2, 4 H), 6.80 (s, 5 H), and 9.85 (s, 1 H) p.p.m.

(*b*) p-$ClC_6H_4(PhSO_2)NOH$. The hydroxylamine (0.53 g, 1.87 mmol) was stirred with an excess of PbO_2 in benzene (100 cm^3) during 24 h. Work-up as in (*a*) yielded p-$ClC_6H_4(PhSO_2)NOSO_2Ph$ (0.20 g, 0.47 mmol, 51%), m.p. 98—99 °C (Found: C, 50.4; H, 4.4; N, 2.9. Calc. for $C_{18}H_{14}ClNO_5S_2$: C, 51.1; H, 3.1; N, 3.3%). Extraction of the residual oil with CS_2 (100 cm^3) yielded 4-chloronitrobenzene (0.10 g, 0.64 mmol, 68%), m.p. and mixed m.p. 81—82 °C. Further extraction with hot ethanol (100 cm^3) afforded 4,4′-dichloroazoxybenzene (0.05 g, 0.19 mmol, 20%), m.p. 156—157 °C (lit.,[8] 158 °C).

TABLE 1

Microanalytical data, yields, and melting points for new $R^1(R^2SO_2)NOH$

		Analysis (%)							
		Found			Calc.				
R^1	R^2	C	H	N	C	H	N	Yield (%)	M.p. (θ_c/°C)
Ph	p-MeC_6H_4	59.6	5.1	5.1	59.3	5.0	5.3	75	121—124
p-MeC_6H_4	p-MeC_6H_4	59.9	5.4	5.2	60.6	5.5	5.1	63	126—128
p-ClC_6H_4	Ph	51.0	3.7	5.2	50.8	3.6	4.9	55	101—103
p-ClC_6H_4	p-$MeOC_6H_4$	50.2	3.9	4.2	49.8	3.9	4.5	52	97—99
Ph	Me	45.3	5.1	7.3	44.9	4.9	7.5	51	91—93

(*c*) p-$ClC_6H_4(p$-$MeOC_6H_4SO_2)NOH$. Oxidation (1.50 g, 4.79 mmol) as above with PbO_2 yielded 4-chloronitrobenzene, 4,4′-dichloroazoxybenzene, and a deep red solid (0.80 g), m.p. 95—97 °C (Found: C, 48.5; H, 3.5; N, 5.3. Calc. for $C_{20}H_{18}ClNO_7S_2$: C, 49.6; H, 3.8; N, 2.9%). Chromatography [SiO_2, 30% tetrahydrofuran (thf) in hexane] of a sample (170 mg) yielded 45 mg of p-$ClC_6H_4(p$-$MeOC_6H_4SO_2)NOSO_2C_6H_4OMe$-$p$ (Found: C, 47.9; H, 6.2; N, 3.5%) and 50 mg of an apparently inseparable mixture of this compound and the radical $(p\text{-}ClC_6H_4)_2NO^{\bullet}$: a_N 9.5, $a_{o,p\text{-H}}$ 1.9, $a_{m\text{-H}}$ 0.8 G;[*,9] m/e 251.998 6 u ($^{12}C_{12}{}^{1}H_8{}^{35}Cl_2{}^{14}N^{16}O$ requires 251.998 3 u). Methanol eluted 30 mg of p-$MeOC_6H_4SO_3H$. Use of 1,4-dioxan as eluant gave as the only isolable product a material of composition $(CH_2OCH_2CH_2O)_n$, identified by accurate mass measurements on a series of ions in its mass spectrum.

(*d*) $Ph(p$-$MeC_6H_4SO_2)NOH$. *In situ* oxidation with PbO_2–C_6H_6 yielded the radical $Ph(p$-$MeC_6H_4SO_2)NO^{\bullet}$.

(*e*) p-$MeC_6H_4(p$-$MeC_6H_4SO_2)NOH$. No radical was detected in the *in situ* oxidation with PbO_2–C_6H_6: from reaction with an excess of aqueous HNO_2, the hydroxylamine was recovered unchanged.

Oxidation of N-*Methylsulphonyl*-N-*phenylhydroxylamine*.—The hydroxylamine (1.80 g, 9.63 mmol) was oxidised with PbO_2 as described previously: work-up afforded 0.9 g of a deep red solid (0.4 g), m.p. 93—94 °C (Found: C, 39.9; H, 4.5; N, 5.7. Calc. for $C_8H_{11}NO_5S_2$: C, 36.2; H, 4.2; N, 5.3%). Hydrogen-1 n.m.r. spectrum: δ 3.05 (s, 3 H), 3.32 (s, 3 H), and 6.9—7.2 (m, 5 H) p.p.m. The residue contained both $PhNO_2$ and $PhNN(O)Ph$.

Oxidation of N-*Benzoyl*-N-*phenylhydroxylamine*.—The hydroxylamine (2.13 g, 10 mmol) was oxidised with PbO_2 in benzene: work-up yielded 0.9 g of crude product, together with a residual oil containing $PhNO_2$ and $PhNN(O)Ph$. A portion (250 mg) of the crude product was chromatographed on SiO_2 (thf–hexane) to yield $Ph(PhCO)NOCOPh$ (50 mg) (Found: C, 74.9; H, 4.9; N, 4.8. Calc. for $C_{20}H_{15}NO_3$: C, 75.7; H, 4.8; N, 4.4%), and $PhCONHPh$ (120 mg), m.p. 161—162 °C (lit.,[10] 161 °C).

N.M.R. Spectra.—Integrated proton spectra ($CDCl_3$ solution) were as expected: methyl chemical shifts were as follows (δ/p.p.m.): $Ph(MeOC_6H_4SO_2)NOH$, 2.97; $ClC_6H_4(MeOC_6H_4SO_2)NOH$, 3.00; $Ph(MeSO_2)NOH$, 2.03; $Ph(MeSO_2)NOSO_2Me$, 3.05 and 3.32.

Carbon-13 n.m.r. spectra were recorded, not only of species $R^1(R^2SO_2)NOH$ and $R^1(R^2SO_2)NOSO_2R^2$ but also of p-$XC_6H_4SO_2Na$, $(p$-$XC_6H_4SO_2)_2NOH$, and $(p$-$XC_6H_4SO_2)_2NOSO_2C_6H_4X$-$p$ (X = H, Me, Cl, F, or OMe), and the chemical shifts (Me_2SO solution) are recorded in Table 2. Assignments, which are to be regarded as tentative only, were based on the following considerations: (*i*) off-resonance decoupling distinguished the resonances due to quaternary carbon atoms from those due to C–H; (*ii*) the resonances of carbon bonded to chlorine were assigned by observation of their long relaxation times; (*iii*) in p-FC_6H_4X species, the resonances were assigned by means of ^nJ(C–F), C^1 and C^2 being distinguished by off-resonance decoupling; (*iv*) use of the approximately additive property [11–13] of substituent effects on chemical shifts, as well as internal comparisons, enabled most other assignments to be made.

Much more important than the detailed assignments, however, is the total number of aromatic carbon resonances observed for each class of compound. Compounds of type $(RSO_2)_2NOH$, $(RSO_2)_2NH$, and $(RSO_2)_3N$ exhibit four resonances only (as do RSO_2NH_2 and RSO_2Na), indicating that the rings are identical in these species: however, $(RSO_2)_2NOSO_2R$, with the exception of $(PhSO_2)_2NOSO_2Ph$ whose spectrum contains only four resonances, exhibit up to eight resonances, indicating *two* types of aromatic ring, consistent with their formulation [3] as *NNO*-trisubstituted

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* Throughout this paper: 1 G = 10^{-4} T.

[7] M. O. Forster, *J. Chem. Soc.*, 1898, **73**, 783.

[8] L. Zechmeister and P. Rom, *Annalen*, 1929, **468**, 117.

[9] E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, 1967, **32**, 3853.

[10] R. Meyer and W. Sundmacher, *Ber.*, 1899, **32**, 2112.

[11] L. F. Johnson and W. C. Jankowski, 'Carbon-13 N.M.R. Spectra,' Wiley, New York, 1972.

[12] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

[13] C.-J. Chang, H. G. Floss, and G. E. Peck, *J. Medicin. Chem.*, 1975, **18**, 505.

TABLE 2

Carbon-13 chemical shifts (δ/p.p.m.)

Compound	Total number of aromatic shifts	C^1	C^2, C^3	C^4	Other
$PhSO_2NH_2$	4	144.8	126.7, 129.6	132.6	
p-$MeC_6H_4SO_2NH_2$	4	143.2	126.7, 130.0	141.8	21.3
$(p$-$MeC_6H_4SO_2)_2NH$	4	142.5	126.7, 129.1	139.7	21.0
$(p$-$ClC_6H_4SO_2)_2NH$	4	139.8	129.6, 130.1	140.4	
$(p$-$MeC_6H_4SO_2)_3N$	4	142.4	127.3, 128.7	141.1	21.0
$PhSO_2Na$	4	156.0	125.9, 131.5	132.9	
p-$MeC_6H_4SO_2Na$	4	153.1	125.8, 131.9	143.3	22.9
p-$ClC_6H_4SO_2Na$	4	154.4	127.8, 131.6	129.7	
p-$FC_6H_4SO_2Na$	4	130.6 [a]	128.4,[b] 118.5 [c]	149.4 [d]	
p-$MeOC_6H_4SO_2Na$	4	157.8	116.8, 130.0	127.9	57.0
$(PhSO_2)_2NOH$	4	140.0	128.6, 129.1	134.6	
$(p$-$MeC_6H_4SO_2)_2NOH$	4	138.9	128.3, 128.7	144.8	21.2
$(p$-$ClC_6H_4SO_2)_2NOH$	4	133.1	127.7, 129.3	140.2	
$(p$-$FC_6H_4SO_2)_2NOH$	4	132.8 [e]	128.1,[f] 114.7 [g]	162.3 [h]	
$(p$-$MeOC_6H_4SO_2)_2NOH$	4	163.9	114.2, 131.1	127.2	55.8
$(PhSO_2)_2NOSO_2Ph$	4		(125.7, 128.1, 129.3, 147.3) [i]		
$(p$-$MeC_6H_4SO_2)_2NOSO_2C_6H_4Me$-$p$	7	138.0	128.1, 129.1 129.8, 129.9	145.1 146.0	20.7 21.1
$(p$-$ClC_6H_4SO_2)_2NOSO_2C_6H_4Cl$-$p$	8	130.2 131.2	127.5, 127.8 129.0, 129.8	146.9 154.4	
$(p$-$FC_6H_4SO_2)_2NOSO_2C_6H_4F$-$p$	7	129.8 133.6	128.0 [j] 114.5 [l] 132.2 [k] 116.6 [m]	166.7 [n]	
$(p$-$MeOC_6H_4SO_2)_2NOSO_2C_6H_4OMe$-$p$	6	163.9	112.8, 114.2 127.1, 131.1	125.9	55.2 55.9
PhNHOH	4	152.2	113.4, 128.7	119.8	
$Ph(PhSO_2)NOH$	8	132.6 142.6	122.6, 128.1 128.6, 129.1	126.9 133.9	
$Ph(p$-$MeC_6H_4SO_2)NOH$	5	139.3 154.6	125.9, 128.9	144.1	21.2
$Ph(PhSO_2)NOSO_2Ph$	12	132.7 140.2 142.1	122.0, 126.0 126.6, 128.1 129.1, 129.6	124.5 127.3 134.9	
PhS(O)OEt	4	144.9	125.2, 129.1	132.1	15.6 61.2
$PhSO_2Et$	4	133.6	128.2, 129.3	133.7	18.1 50.6

[a] ^4J(CF) 9.4 Hz. [b] ^3J(CF) 8.9 Hz. [c] ^2J(CF) 22.2 Hz. [d] ^1J(CF) 240.1 Hz. [e] ^4J(CF) 10.6 Hz. [f] ^3J(CF) 8.5 Hz. [g] ^2J(CF) 21.7 Hz. [h] ^1J(CF) 245.1 Hz. [i] See text. [j] ^3J(CF) 8.3 Hz. [k] ^3J(CF) 10.3 Hz. [l] ^2J(CF) 21.5 Hz. [m] ^2J(CF) 23.7 Hz. [n] ^1J(CF) 255.3 Hz.

hydroxylamines rather than as amine oxides $(RSO_2)_3NO$: two CH_3 resonances (intensity ratio 2 : 1) were previously observed [1] where R = p-$MeOC_6H_4$, but not p-MeC_6H_4, and two ^{19}F resonances (ratio 2 : 1) were found [1] when R = p-FC_6H_4, consistent with the ^{13}C results reported here.

The compound $Ph(PhSO_2)NOH$ exhibits eight ^{13}C resonances, but $Ph(PhSO_2)NOSO_2Ph$ exhibits 12, indicating that all the three rings are distinct in this compound, which is therefore also an *NNO*-trisubstituted hydroxylamine.

E.S.R. Spectra.—Apparently analytically pure samples of $R^1(PhSO_2)NOSO_2Ph$ (R^1 = Ph or p-ClC_6H_4), despite giving sharp well resolved ^1H and ^{13}C n.m.r. spectra, exhibit e.s.r. spectra in solution, having a_N of 11.5 and 11.2 G respectively, which are assignable [5] to the radicals $R^1(PhSO_2)NO^{\bullet}$. Similarly, samples of $(p$-$XC_6H_4SO_2)_2NOSO_2C_6H_4X$-$p$ (X = H, Me, Cl, or F, but not MeO) exhibit spectra consisting, for X = H, Me, or Cl, of simple 1 : 1 : 1 triplets; when X = F a splitting (0.6 G) due to F is also observed: these spectra are assigned to the radicals $(p$-$XC_6H_4SO_2)_2NO^{\bullet}$. No discernable coupling of the unpaired electron with the hydrogen nuclei in an RSO_2N group was observed in any of the spectra. Table 3 lists the a values. The oxidation of $Ph(MeSO_2)NOH$ yielded an inseparable mixture of $Ph(MeSO_2)NOSO_2Me$ and a radical whose spectrum consisted of a broad 1 : 1 : 1 triplet, a_N = 12.5 G, which we assign to $Ph(MeSO_2)NO$.

From the oxidation of p-$ClC_6H_4(p$-$MeOC_6H_4SO_2)NOH$, the only radical detected is $(p$-$ClC_6H_4)_2NO^{\bullet}$: a_N 9.5 (lit.,[9] 9.4), $a_{o,p\text{-H}}$ 1.9; $a_{m\text{-H}}$ 0.89 G. We have been unable to isolate pure samples of this radical, even though it appears to be formed in substantial yield (>10%) in the oxidation of p-ClC_6H_4-$(p$-$MeOC_6H_4)NOH$: its decomposition path has been described.[14]

TABLE 3

E.s.r. data

(*a*) Radicals $(p$-$XC_6H_4SO_2)_2NO^{\bullet}$

X	a_N [a]/G	Other
H	12.0	
Me	11.0	
Cl	10.5	
F	10.5	a_F 0.6 G
OMe	N.o.[b]	

(*b*) Radicals $R^1(R^2SO_2)NO^{\bullet}$

R^1	R^2	a_N/G
Ph	Ph	11.5
Ph	p-MeC_6H_4	12.2
p-ClC_6H_4	Ph	11.2
Ph	Me	12.5

[a] a values are believed to be correct to within ±0.1 G. [b] n.o. = Not observed.

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[14] K. Tokumaru, H. Sakuragi, and O. Simomura, *Tetrahedron Letters*, 1964, 3945.

Infrared Spectra.—The compounds $R^1(R^2SO_2)NOH$ and $R^1(R^2SO_2)NOSO_2R^2$ all contain a band at *ca.* 1 080 cm^{-1} assignable [3] to ν(N–O); $R^1(R^2SO_2)NOH$ all contain ν(O–H) and $R^1(R^2SO_2)NOSO_2R^2$ all contain ν(S–O). These diagnostic frequencies (Table 4) support the formulations of $R^1(R^2SO_2)NOH$ as *NN*- (rather than *NO*-) disubstituted hydroxylamines, and of $R^1(R^2SO_2)NOSO_2R^2$ as *NNO*-trisubstituted hydroxylamines rather than as amine oxides.

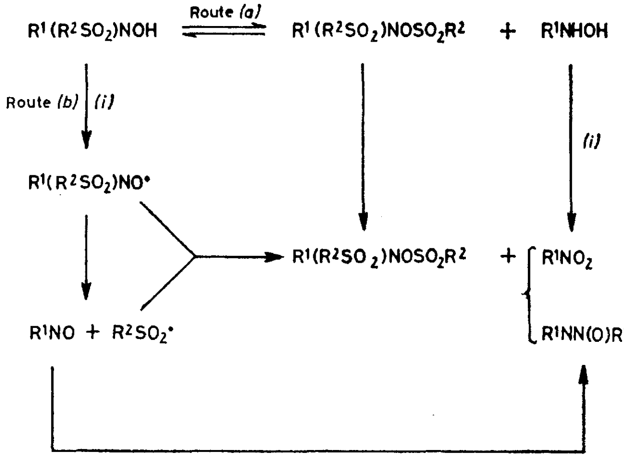
TABLE 4

Diagnostic i.r. bands (cm^{-1}) for $R^1(R^2SO_2)NOH$ [ν(O–H)] and $R^1(R^2SO_2)NOSO_2R^2$ [ν(S–O)]

R^1	R^2	ν(O–H)	ν(S–O)
Ph	Ph	3 380	820
p-ClC_6H_4	Ph	3 375	830
p-ClC_6H_4	p-$MeOC_6H_4$	3 302	825
Ph	Me	3 310	850

RESULTS AND DISCUSSION

The hydroxylamine $Ph(PhSO_2)NOH$ is oxidised by PbO_2–C_6H_6 and $Pb[O_2CMe]_4$–CH_2Cl_2 to yield $Ph(PhSO_2)NOSO_2Ph$ and a mixture of nitrobenzene and azoxybenzene. As with the oxidation [3] of $(RSO_2)_2NOH$ to yield $(RSO_2)_2NOSO_2R$ and nitrate, two routes to the products are plausible (Scheme). Route (*a*), which involves a redistribution equilibrium, may be eliminated by the observation that although aqueous HNO_2 will oxidise RNHOH to a mixture of RNO_2 and RNN(O)R (R = Ph or p-ClC_6H_4), it does not oxidise $Ph(PhSO_2)NOH$ to $Ph(PhSO_2)NOSO_2Ph$, but merely nitrosates the *N*-phenyl ring to yield p-$ONC_6H_4(PhSO_2)NOH$: when the 4-position of this ring is blocked, as by Cl or Me, the hydroxylamine $R^1(R^2SO_2)NOH$ is recovered unchanged.



SCHEME (*i*) oxidation

Corroborative evidence for route (*b*) is obtained by the observation, when $R^1 = R^2 = Ph$, that apparently pure samples of $Ph(PhSO_2)NOSO_2Ph$ are contaminated with small quantities of the radical $Ph(PhSO_2)NO^{\bullet}$. This radical has been previously detected by Wajer *et al.*,[5] who only investigated the paramagnetic product of the oxidation of $Ph(PhSO_2)NOH$. Balaban and Negoita [15] have also studied the paramagnetic product of the oxidation of this hydroxylamine and they report that in dioxan the spectrum of $Ph(PhSO_2)NO$ lasts for only a few minutes, and is quickly replaced by that of $PhN(NO)O^{\bullet}$, and then more slowly by that of $Ph_2NO^{\bullet}$. In contrast, we observe identical spectra from isolated samples of $Ph(PhSO_2)NOSO_2Ph$ (oxidation time 24 h) and from *in situ* oxidation of $Ph(PhSO_2)NOH$: furthermore, the mechanistic scheme postulated by Balaban and Negoita requires formation of Ph_2SO_2 which we do not find, but not of $PhNO_2$ or PhNN(O)Ph both of which we isolate. Although their reaction was reported to be conducted in 1,4-dioxan, we have found that this solvent is polymerised by aminyl oxides (see Experimental section). Similarly, we find that apparently analytically pure samples of p-$ClC_6H_4(PhSO_2)NOSO_2Ph$ contain the radical p-$ClC_6H_4(PhSO_2)NO^{\bullet}$: the identical radical is obtained by *in situ* oxidation of p-$ClC_6H_4(PhSO_2)NOH$, again in disagreement with Balaban and Negoita.

However, when $R^1 = p$-ClC_6H_4 and $R^2 = p$-$MeOC_6H_4$, the only radical detected was $(p$-$ClC_6H_4)_2NO^{\bullet}$, but again no sulphones were observed, so that the scheme of Balaban and Negoita cannot be confirmed: nevertheless, the formation of this radical is most unexpected.

The observation of radicals $(RSO_2)_2NO^{\bullet}$ in apparently pure samples of $(RSO_2)_2NOSO_2R$ supports the analogous route (*b*) suggested [3] for the oxidation of $(RSO_2)_2NOH$, as it seems extremely unlikely that $(RSO_2)_2NOSO_2R$ could undergo spontaneous homolysis in solution.

The compounds $R^1(R^2SO_2)NOSO_2R^2$ all contain a band in their i.r. spectra assignable to ν(S–O) which supports their formulation as *NNO*-trisubstituted hydroxylamines. This formulation is further supported by n.m.r. spectroscopy in the cases of $Ph(MeSO_2)NOSO_2Me$, which exhibits two distinct methyl resonances (δ 3.05 and 3.32 p.p.m.) in its ^1H spectrum, and of $Ph(PhSO_2)NOSO_2Ph$ which exhibits 12 aromatic resonances in its ^{13}C spectrum (Table 2); $Ph(PhSO_2)NOH$ in contrast exhibits only eight such resonances as would the amine oxide $Ph(PhSO_2)_2NO$. Similar support for the *NNO*-trisubstituted hydroxylamine constitutions of compounds $(RSO_2)_2NOSO_2R$ is derived from their ^{13}C n.m.r. spectra (see Table 2 and Experimental section).

Similar to the hydroxylamines $R^1(R^2SO_2)NOH$ is the compound Ph(PhCO)NOH, oxidation of which yields Ph(PhCO)NOCOPh, analogous to $R^1(R^2SO_2)NOSO_2R^2$, and also PhCONHPh, in addition to the usual $PhNO_2$ and PhNN(O)Ph. Our observations confirm those of Forrester,[16] including the isolation of the unexpected PhCONHPh. An apparently pure sample of Ph(PhCO)NOCOPh exhibited an e.s.r. spectrum identical to that of the known [17] radical $Ph(PhCO)NO^{\bullet}$; this supports a scheme analogous to that proposed for the oxidation of the sulphonylhydroxylamines.

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[15] A. T. Balaban and N. Negoita, *Rev. Roumaine Chem.*, 1972, **17**, 227.

[16] A. R. Forrester, Ph.D. Thesis, Aberdeen University, cited in ref. 2.

[17] H. G. Aurich and F. Baer, *Tetrahedron Letters*, 1965, 3879.