Sulphur–Nitrogen Compounds: the Preparation, Oxidation, and Decomposition of *NN*-Bis(arylsulphonyl)hydroxylamines

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NN-Bis(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOH$, have been prepared (X = H, Me, MeO, Cl, and F) by reaction of the corresponding benzenesulphinic acids with nitrous acid. Oxidation of the bis species with PbO_2, silver(I,III) oxide, AgO, MnO_2, $Pb(O_2CMe)_4$, or nitric acid yields *NNO*-tris(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$, but HNO_2 and *m*-chloroperbenzoic acid do not react. Infrared and n.m.r. spectra show that the tris species are hydroxylamines, R_2NOR, rather than amine oxides, R_3NO. Early work on similar compounds has been reinvestigated.

As part of an investigation of nitroxyls, routes have been sought to neutral analogues of Fremy's radical ion of the form $(RSO_3)_2NO$ and $(RSO_2)_2NO$: one possible approach to the latter class of compounds, bis(sulphonyl)-aminyl oxides, is the oxidation of the analogous hydroxylamines $(RSO_2)_2NOH$, and work on the preparation, oxidation, and decomposition of these species is reported here.

Bis(arylsulphonyl)hydroxylamines appear to have been first prepared, although not recognised as such, by reaction of arenesulphinic acids with nitrous acid [1] or with oxides of nitrogen; [2,3] the action of fuming nitric acid on arenesulphinic acids was reported [4] to give tris-(arylsulphonyl)amine oxides. Hinsberg claimed [5] the preparation of bis(phenylsulphonyl)hydroxylamine by the action of HNO_2 on benzenesulphonamide, while Piloty [6] obtained from the reaction of aqueous iron(III) chloride and *N*-(phenylsulphonyl)hydroxylamine a substance which he described as *NN*-bis(phenylsulphonyl)-hydroxylamine. More recently, bis(arylsulphonyl)-hydroxylamines have been obtained from the decomposition of aryl sulphones with HNO_3,[7] by the reaction [8] of HNO_2 with *N*-(arylsulphonylamino)-piperidine and -pyrrolidine, and by the reaction [9] of arenesulphinic acids with nitroalkanes. We have refnvestigated the earlier work,[1-6] and have developed simple preparations of *NN*-bis(arylsulphonyl)hydroxylamines.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory of this Department. Nuclear magnetic resonance spectra were recorded on Varian EM-360, HA-100, and XL-100 spectrometers, e.s.r. spectra on a Decca X-3 instrument, i.r. spectra on a Perkin-Elmer 237 instrument, and mass spectra on an A.E.I. MS902 instrument.

Materials.—Ethanol, propan-1-ol, and methylene chloride were dried over flamed-out molecular sieves. Diethyl ether

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[1] R. Otto and H. Ostrop, *Annalen*, 1867, **141**, 370.

[2] R. Otto and V. Gruber, *Annalen*, 1868, **145**, 18.

[3] W. Konigs, *Ber.*, 1878, **11**, 616.

[4] W. Konigs, *Ber.*, 1878, **11**, 1588.

[5] O. Hinsberg, *Ber.*, 1894, **27**, 598.

[6] O. Piloty, *Ber.*, 1896, **29**, 1560.

[7] H. R. Henze and N. E. Artman, *J. Org. Chem.*, 1957, **22**, 1410.

[8] P. A. S. Smith and H. G. Pars, *J. Org. Chem.*, 1959, **24**, 1325.

[9] G. Kresze and W. Kort, *Ber.*, 1961, **94**, 2624.

TABLE 1

Microanalyses, melting points, and yields of *NN*-bis(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOH$

	Analysis (%)							
	Found			Calc.				
X	C	H	N	C	H	N	M.p. (θ_c/°C)	Yield (%)
H	45.9	3.4	4.2	45.9	3.5	4.5	125	86
Me	49.0	4.3	3.8	49.2	4.4	4.1	126	50
Cl	36.3	2.4	3.3	37.7	2.4	3.7	128	91
MeO	41.8	4.2	3.4	45.0	4.1	3.7	74—75	61
F	Unstable			41.0	2.6	4.0	decomp.	47

was repeatedly refluxed over calcium hydride and stored over the same reagent: other solvents were dried over sodium wire. Arenesulphonyl chlorides were commercial products and were used as received.

Preparation of Sodium Arenesulphinates.—Reduction of benzenesulphonyl chloride with sodium amalgam [10] or sodium sulphite [11] gave yields of 30—50%: no product was obtained using sodium sulphide as reductant.[12] Reduction with zinc in propan-1-ol [13] gave 87% yield. Reduction of toluene-*p*-sulphonyl chloride with $Na_2[SO_3]$ gave 32% of the sodium sulphinate, zinc reduction gave 91%, and lithium tetrahydridoaluminate [14] gave 93%. Sodium *p*-chlorobenzenesulphinate and sodium *p*-methoxybenzenesulphinate were prepared by zinc reduction of the arenesulphonyl chlorides in yields of 91 and 98% respectively: small quantities of the aryl sulphones, identified mass spectrometrically, were also formed in these reductions. Sodium *p*-fluorobenzenesulphinate was prepared [15] from fluorobenzene. No conditions were found under which *p*-nitrobenzenesulphonyl chloride could be selectively reduced to the sulphinate, without concomitant reduction of the nitro-group.

TABLE 2

Preparation, microanalysis, melting points, and yields of *NNO*-tris(arylsulphonyl)hydroxylamines, $(p\text{-}XC_6H_4SO_2)_2NOSO_2\text{-}C_6H_4X\text{-}p$

			Analysis (%)							
			Found			Calc.				
X	Amount (mmol) of $(p\text{-}XC_6H_4SO_2)_2NOH$	Amount (mmol) of PbO_2	C	H	N	C	H	N	M.p. (θ_c/°C)	Yield (%)
H	5.0	7.2	47.6	3.3	3.0	47.4	4.0	3.1	89—91	72
Me	3.0	8.4	50.8	4.6	2.9	50.9	4.3	2.8	183—184	71
Cl	2.6	20	38.6	2.9	2.2	38.8	2.2	2.5	132—135	52
MeO	1.6	8.4	46.4	4.1	2.4	46.4	3.9	2.6	107—108	50
F	5.2	20	43.0	2.7	2.4	42.6	2.4	2.8	123—125	65

Preparation of NN-*Bis(arylsulphonyl)hydroxylamines.*—Typically, the sodium arenesulphinate (0.02 mol) and sodium nitrite (0.69 g, 0.01 mol) were dissolved in distilled water (50 cm^3) and concentrated hydrochloric acid (3 cm^3) was added dropwise. The product was filtered off, washed with water, and dried. Yields, microanalytical data, and melting points (uncorrected) are recorded in Table 1. The *p*-fluoro-derivative was too unstable either for accurate microanalysis or for melting-point determination. The compounds were stored at −30 °C.

Oxidation of NN-*Bis(arylsulphonyl)hydroxylamines with Lead*(IV) *Oxide and Other Oxidants.*—In a typical oxidation, the hydroxylamine was stirred during 24 h with excess of lead(IV) oxide in methylene chloride (*ca.* 100 cm^3). The mixture was then centrifuged: evaporation of the solvent yielded the crude tris(arylsulphonyl)hydroxylamine. The products were recrystallised twice from toluene. The solid residue was washed with water: the aqueous washings gave a positive test for nitrate, but a test for nitrite was negative. A blank oxidation of hydroxylammonium chloride in methylene chloride gave nitrate and no nitrite. Table 2 records the stoicheiometries employed, together with the yields, melting points, and microanalytical data. The results of other oxidation procedures are summarised in Table 3: the tris products were identical (microanalysis, m.p., and mixed m.p.) with the products from oxidation by PbO_2.

Reaction of Benzenesulphinic Acid with Fuming Nitric Acid.—A solution of sodium benzenesulphinate (4.0 g, 0.024 mol) in water (100 cm^3) was treated with concentrated HCl (0.02 cm^3): the resulting precipitate of benzenesulphinic acid was filtered off and dried, then stirred during 18 h with fuming HNO_3 (s.g. 1.51; 10 cm^3). Filtration of the resulting solid, followed by recrystallisation from toluene, yielded tris(phenylsulphonyl)hydroxylamine (2.10 g, 4.6 mmol, 58%), identical (microanalysis, m.p., and mixed m.p.) with that obtained by oxidation of *NN*-bis(phenylsulphonyl)hydroxylamine.

TABLE 3

Formation of tris(arylsulphonyl)hydroxylamines by oxidation of *NN*-bis(arylsulphonyl)hydroxylamines (+, formed; —, not formed)

Oxidant	X = H	Me	Cl	MeO	F
PbO_2–CH_2Cl_2	+	+	+	+	+
AgO–CH_2Cl_2		+	+		
PbO_2–C_6H_6		+	+		
AgO–C_6H_6		+	+		
$Pb(O_2CMe)_4$–CH_2Cl_2		+			
MnO_2–CH_2Cl_2 [a]		+			
PbO_2–$K_2[CO_3]$ (aq)		—			
AgO–$K_2[CO_3]$ (aq)		—			
$Na[NO_2]$–HCl (aq)		—			
SeO_2–CH_2Cl_2		*b*			
HNO_3–$MeCO_2H$		+ [c]			
m-$ClC_6H_4CO_3H$–Et_2O		—			

[a] J. Attenbarrow, A. F. B. Cameron, J. M. Chapman, R. M. Evans, B. A. Hens, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094. [b] No homogeneous product isolable. [c] Evaporation of the filtrate, after removal of product, yielded toluene-*p*-sulphonic acid.

Preparation and Reactions of N-*(Phenylsulphonyl)hydroxylamine.*—Benzenesulphonyl chloride (35.4 g, 0.20 mol) was added dropwise to a solution of hydroxylammonium chloride (13.9 g, 0.20 mol) in ethanol (150 cm^3) through which ammonia was bubbled: when the addition was complete, passage of ammonia was continued for another

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[10] S. Gabriel and A. Deutsh, *Ber.*, 1880, **13**, 388.

[11] F. C. Whitmore and F. H. Hamilton, *Org. Synth.*, 1932, Coll. Vol. 1, 7.

[12] V. Migrdichian, ' Organic Syntheses,' Reinhold, New York, 1957, vol. 2, p. 1701.

[13] H. Gilman, E. W. Smith, and H. J. Oatfield, *J. Amer. Chem. Soc.*, 1934, **56**, 1412.

[14] L. Field and F. A. Gunwald, *J. Org. Chem.*, 1951, **16**, 946.

[15] R. M. Hann, *J. Amer. Chem. Soc.*, 1935, **57**, 2167.

10 min, before removal of ammonium chloride by filtration. Removal of the solvent yielded the product which was recrystallised from acetonitrile (12.1 g, 0.07 mol, 35%; m.p. 124—126 °C) (Found: C, 41.5; H, 4.6; N, 8.9. $C_6H_7NO_3S$ requires C, 41.8; H, 4.1; N, 8.1%). The hydroxylamine (3.46 g, 0.020 mol) and $FeCl_3$ (3.25 g, 0.020 mol) were stirred in aqueous solution during 15 h: after centrifuging, and removal of the solvent, the hydroxylamine was recovered unchanged. Similarly, the hydroxylamine was recovered unchanged after stirring during 5 h with a two-fold molar excess of sodium hydroxide; no sodium benzenesulphinate was found.[16]

Reactions of Benzenesulphonamide with Aqueous Nitrous Acid.—(i) Benzenesulphonamide (3.14 g, 0.02 mol) and sodium nitrite (2.07 g, 0.03 mol) were dissolved in water (100 cm^3) and concentrated HCl (9 cm^3) was slowly added. Nitrogen oxides were evolved: after 1 h, the solid removed by filtration was the unchanged sulphonamide. (ii) A reaction (2 : 3 ratio) in ethanol gave only unchanged sulphonamide. (iii) A 1 : 1 molar ratio of the reactants, after stirring during 24 h at room temperature in ethanol, gave unchanged sulphonamide and diphenyl disulphone, $(PhSO_2)_2$, identified mass spectrometrically.

Attempted Reactions of Benzenesulphonamide with Nitric Acid.—Aliquot portions (3.1 g, 0.02 mol) of benzenesulphonamide were treated during 24 h with HNO_3 as follows: (i) concentrated HNO_3 (10 cm^3) + water (10 cm^3); (ii) concentrated HNO_3 (10 cm^3); (iii) fuming HNO_3 (10 cm^3). A quantitative recovery of unchanged benzenesulphonamide was achieved in each case.

Reaction of Toluenesulphinic Acid with Excess of Nitrous Acid.—A solution of sodium toluene-*p*-sulphinate (2.5 g, 0.01 mol) in water (50 cm^3) was treated with concentrated HCl (3 cm^3): the toluene-*p*-sulphinic acid was filtered off, washed, and added to a solution of $Na[NO_2]$ (1.38 g, 0.02 mol) in water (200 cm^3), to which concentrated HCl (6 cm^3) was then added: the mixture was stirred during 24 h. *NN*-Bis(*p*-tolylsulphonyl)hydroxylamine (1.0 g, 2.9 mmol, 58%) was filtered off and recrystallised from toluene: it was identical (microanalysis, m.p., and mixed m.p.) with samples obtained earlier. No tris(*p*-tolylsulphonyl)hydroxylamine was obtained.

Reactions of NN-*Bis*(p-*tolylsulphonyl*)*hydroxylamine with Toluene*-p-*sulphinic Acid*.—(*a*) Toluene-*p*-sulphinic acid (1.20 g, 8 mmol) in glacial acetic acid (75 cm^3) was added dropwise to a solution of the hydroxylamine (2.0 g, 6 mmol) in acetic acid (150 cm^3). The mixture was warmed to 60 °C for 5 h: oxides of nitrogen were evolved. After another 24 h at room temperature, the solvent was removed; the solid product was recrystallised from toluene, and identified as toluene-*p*-sulphonic acid by its m.p. (103 °C; lit.,[17] 104—106 °C), and mass spectrum. No tris(*p*-tolylsulphonyl)hydroxylamine or amine [16] was found. (*b*) An identical reaction was carried out under dry nitrogen. No oxides of nitrogen were evolved. The bis(*p*-tolylsulphonyl)hydroxylamine was recovered unchanged.

Reaction of NN-*Bis*(p-*tolylsulphonyl*)*hydroxylamine with Toluene*-p-*sulphonyl Chloride*.—Toluene-*p*-sulphonyl chloride (1.37 g, 7.2 mmol) in glacial acetic acid (75 cm^3) was stirred into a solution of the hydroxylamine (2.45 g, 7.2 mmol) and pyridine (0.57 g, 7.2 mmol) in glacial acetic acid (75 cm^3). After 24 h at room temperature, the mixture was reduced to small volume and extracted with benzene (2 × 100 cm^3). The benzene layer was washed well with water, dried over anhydrous sodium sulphate for 24 h, and evaporated to yield an oil which crystallised slowly: extraction with diethyl ether gave unchanged toluene-*p*-sulphonyl chloride. Recrystallisation of the residue from toluene gave tris(*p*-tolylsulphonyl)hydroxylamine (0.52 g, 1.1 mmol, 15%) identical (microanalysis, m.p., and mixed m.p.) with samples obtained earlier.

Decomposition of NN-*Bis*(*arylsulphonyl*)*hydroxylamines*, $(p\text{-}XC_6H_4SO_2)_2NOH$.—Aliquot portions (0.1 g) of each compound were placed in ampoules, which were subsequently evacuated and allowed to stand at room temperature during 24 h. Dry air was admitted, followed after another 24 h by moist (ambient) air. Any change was monitored at each step. (i) X = H. The compound is stable in dry air; in moist air nitrogen oxides were evolved. Extraction with water removed benzenesulphonic acid, leaving tris(phenylsulphonyl)hydroxylamine, identical with previous samples. (ii) X = *p*-Me and *p*-Cl. No decomposition was observed. (iii) X = *p*-MeO. The compound is stable in dry air; in moist air decomposition occurred without the evolution of nitrogen oxides to give an intractable black tar. (iv) X = *p*-F. The compound is stable in dry air, but in the presence of moisture it decomposed very rapidly with evolution of nitrogen oxides. Extraction of the residue with water removed *p*-fluorobenzenesulphonic acid, identified by mass spectrometry and as its sodium salt (Found: C, 35.0; H, 2.5. $C_6H_4FNaO_3S$ requires C, 36.4; H, 2.1%), leaving tris(*p*-fluorophenylsulphonyl)hydroxylamine, identical with earlier samples.

Decomposition of Tris(*arylsulphonyl*)*hydroxylamines*.—The procedure used for the bis derivatives was employed: all the compounds were stable to dry air. When X = H, *p*-Me, or MeO no change was found after exposure to moist air for 21 d; when X = *p*-Cl or *p*-F, exposure to moist air over a period of weeks caused slow loss of nitrogen oxides and accumulation of the sulphonic acid $p\text{-}XC_6H_4SO_3H$.

Infrared Spectra.—The i.r. spectra of both bis and tris species are consistent with the constitutions postulated: all the spectra contained a strong band at *ca.* 1 080 cm^{-1} identified as ν(N–O) by analogy with 2-(1-hydroxyaminoethyl)quinoline-4-carboxylic acid which contains a strong band at 1 040 cm^{-1}, whereas 2-(1-aminoethyl)quinoline-4-carboxylic acid does not.[18] The principal difference between the spectra of the two series is the presence of ν(O–H) only in the bis series and of ν(S–O) only in the tris series (see Table 4).

N.M.R. Spectra.—The proton spectra (C_6D_6) of the bis derivatives are entirely as expected. In the spectra of the tris derivatives, two methyl resonances in the intensity ratio 2 : 1 were observed at *ca.* δ 3.01 p.p.m. when X = MeO, separated by 2.3 Hz and each having $\nu_{\frac{1}{2}} = 0.6$ Hz. When X = Me, only a single methyl resonance could be resolved at δ 1.77 p.p.m. having $\nu_{\frac{1}{2}} = 2.0$ Hz; however, it seems unlikely that this absorption conceals two unresolved methyl resonances since in the analogous bis compound $\nu_{\frac{1}{2}}$ for the methyl resonance is also 2.0 Hz at δ 1.73 p.p.m. When X = F, two resonances with an intensity ratio 2 : 1 were observed in the ^{19}F spectrum (proton decoupled) at -100.90_4 (1 F) and -101.02 (2 F) p.p.m. (CCl_3F), a separation of 11.00 Hz.

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[16] E. von Meyer, *J. prakt. Chem.*, 1901, **63**, 175.

[17] A. F. Holleman and P. Caland, *Ber.*, 1911, **44**, 2505.

[18] Thermodynamics Research Centre Data Project, Infrared Spectral Data, Texas A and M. University, College Station, Texas, 1974, vol. 1.

E.S.R. Spectra.—*NN*-Bis(*p*-tolylsulphonyl)hydroxylamine was held at room temperature during 6 h with an excess of PbO_2 in benzene or methylene chloride. The solution was then filtered into an e.s.r. tube, carefully degassed, and the tube sealed. The solution showed a strong e.s.r. spectrum, comprising a single rather broad absorption with partially resolved fine structure; no coupling due to ^{14}N was apparent.

TABLE 4

Diagnostic i.r. frequencies in $(p\text{-}XC_6H_4SO_2)_2NOH$ and $(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$

		X = H	Me	Cl
$(p\text{-}XC_6H_4SO_2)_2NOH$	$\bar{\nu}(OH)$ (cm^{-1})	3 300	3 280	3 200
$(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$	$\bar{\nu}(SO)$ (cm^{-1})	850	815	825
		MeO	F	
$(p\text{-}XC_6H_4SO_2)_2NOH$	$\bar{\nu}(OH)$ (cm^{-1})	3 440	3 400	
$(p\text{-}XC_6H_4SO_2)_2NOSO_2C_6H_4X\text{-}p$	$\bar{\nu}(SO)$ (cm^{-1})	850	815	

RESULTS AND DISCUSSION

Arenesulphinic acids react with aqueous HNO_2 to give *NN*-bis(arylsulphonyl)hydroxylamines [equation (1)].

$$2XC_6H_4SO_2H + HNO_2 \longrightarrow (XC_6H_4SO_2)_2NOH + H_2O \quad (1)$$

$$(X = H, p\text{-Me}, p\text{-Cl}, p\text{-MeO, or } p\text{-F})$$

These hydroxylamines are white crystalline solids, stable in dry air; microanalyses, yields, and m.p.s are recorded in Table 1. The yield is essentially independent of the quantity of $Na[NO_2]$ used, provided that at least the stoicheiometric quantity is present. Support for the *NN*-substitution is provided by the i.r. spectra which all contain ν(OH).

A number of methods for the reduction of arenesulphonyl chlorides have been recorded.[10-14] The most satisfactory in our hands is the use of zinc dust in propan-1-ol:[13] this gave yields ranging from 87% when X = H to 98% when X = *p*-MeO. When X = *p*-Cl or *p*-MeO, small quantities of diaryl sulphone were also produced during the reduction, possibly according to equation (2) (R = aryl).

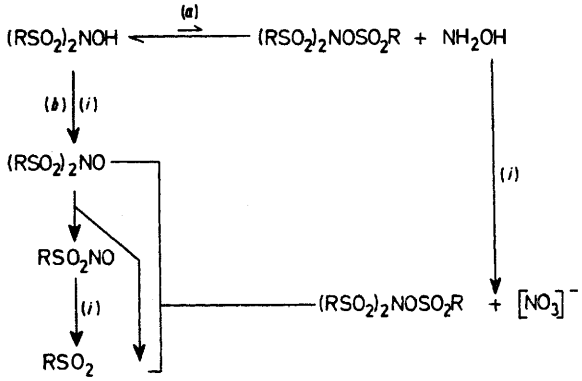
$$RSO_2Na + RSO_2Cl \longrightarrow NaCl + SO_2 + R_2SO_2 \quad (2)$$

A wide variety of oxidising agents were tested in the hope of effecting oxidation of the *NN*-bis(arylsulphonyl)hydroxylamine to the corresponding aminyl oxides equation (3). In methylene chloride, PbO_2 reacted

$$(p\text{-}XC_6H_4SO_2)NOH \longrightarrow (p\text{-}XC_6H_4SO_2)_2NO \quad (3)$$

with each of the bis species to yield *NNO*-tris(arylsulphonyl)hydroxylamines and nitrate. Two of the *NN*-bis(arylsulphonyl)hydroxylamines, having X = *p*-Me and *p*-Cl, were treated with a number of oxidants. When X = *p*-Me, the same tris derivative was obtained when the oxidising agent was silver(I,III) oxide, AgO, in either methylene chloride or benzene, PbO_2 in benzene, lead(IV) acetate in methylene chloride, or manganese(IV) oxide in methylene chloride; aqueous PbO_2 or AgO, excess of HNO_2, and *m*-chloroperbenzoic acid had no action on this bis compound. When X = *p*-Cl, the tris species was also produced by the action of PbO_2 in benzene, and AgO in either benzene or methylene chloride.

Two plausible routes from $(RSO_2)_2NOH$ to $(RSO_2)_2$-$NOSO_2R$ (R = aryl) are outlined in the Scheme. The failure of certain oxidants to generate *NNO*-tris(arylsulphonyl)hydroxylamines allows route (*a*) to be ruled out. Nitrous acid reacts rapidly with hydroxylamine to yield dinitrogen oxide,[19] and PbO_2, AgO, and *m*-chloroperbenzoic acid all oxidise hydroxylamine to nitrate under conditions in which they fail to convert *NN*-bis(arylsulphonyl)hydroxylamines into the tris derivatives; excess of HNO_2 will not convert toluene-*p*-sulphinic acid or *NN*-bis(*p*-tolylsulphonyl)hydroxylamine to the tris compound. The alternative route (*b*) involves a reversal of the spin-trapping reaction to give a nitrosyl arenesulphinate as an intermediate: to the best of our knowledge, this class of compound has yet to be described, and the preparation is now under investigation. Some support for this route is drawn from e.s.r. observations: PbO_2 and *NN*-bis(*p*-tolylsulphonyl)hydroxylamine react to give a free-radical intermediate, but with the apparatus available we were unable to identify this species conclusively. It is probably not a aminyl oxide, since no coupling to ^{14}N is observed, and the toluene-*p*-sulphonyl radical, $p\text{-}MeC_6H_4SO_2$, which has been observed by Waters[20] and by Davies,[21] is probably too short-lived.



SCHEME R = Aryl. (*i*) Oxidation

The tris derivatives are believed to be *NNO*-trisubstituted hydroxylamines rather than *NNN*-trisubstituted amine oxides as described by earlier workers[1,3,4,16] on the grounds of their i.r. spectra, which all contain ν(S–O), and their n.m.r. spectra which show evidence of two types of benzenoid group when X = MeO and F; no conclusive n.m.r. evidence was obtained in the case of X = Me. The amine oxide structure may also be discounted on theoretical grounds. The nitrilotrisulphonate ion $[N(SO_3)_3]^{3-}$ is planar at nitrogen[22]

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[19] R. Nast and I. Föppl, *Z. anorg. Chem.*, 1950, **263**, 310.

[20] M. McMillan and W. A. Waters, *J. Chem. Soc.* (*B*), 1966, 422.

[21] A. G. Davies, B. P. Roberts, and B. R. S. Sanderson, *J.C.S. Perkin II*, 1973, 626.

[22] J. V. Tillak and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1970, 1637.

with an S $\cdots$ S distance of 2.96 Å, approximately equal to the 2.90 Å expected[23] in the hard-atom approximation, and it may be supposed that $N(SO_2R)_3$ would be similar *although* with a shorter N–S and hence shorter S $\cdots$ S distance. If the NS_3 fragment is planar largely because of S $\cdots$ S repulsions, then an increase in the co-ordination number of the nitrogen, as in the formation of the amine oxide $(RSO_2)_3NO$, which would be accompanied by a change in the geometry of the nitrogen atom from trigonal planar to approximately tetrahedral, will only increase the steric compression of the sulphur atoms and consequently increase the total potential energy.

It is probable that the nitrogen atom even in a bis- or tris-(arylsulphonyl)hydroxylamine has almost planar geometry. In Fremy's radical di-anion $[(SO_3)_2NO]^{2-}$, the S_2NO fragment is planar[24] with O–N and N–S distances of 1.28 and 1.66 Å respectively; the distances, and hence angles, assuming the hard-atom approximation,[24] in species such as $(RSO_2)_2NOH$ and $(RSO_2)_2$-$NOSO_2R$ can be estimated from those in Fremy's anion, and from those in the related pair of molecules bis(trifluoromethyl)aminyl oxide, $(CF_3)_2NO$, and *NN*-bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOH$. In $(CF_3)_2NO$, the C–N and N–O distances are[25] 1.441 and 1.26 Å respectively, while in $(CF_3)_2NOH$ these distances are[26] 1.435 and 1.399 Å respectively: if a roughly similar change in the N–O distance occurs in the sulphur species, that in the bis- and tris-(arylsulphonyl)hydroxylamines may be expected to be *ca.* 1.41 Å, with an N–S distance of *ca.* 1.65 Å. Assuming hard-atom non-bonded distances of 2.90 Å for S $\cdots$ S and 2.58 Å for S $\cdots$ O, the SNS and SNO angles are then expected to be 123 and 114.7° respectively, giving a sum of angles at nitrogen of 352.4°, much larger than the 331.8° observed[27] in trimethylamine. It is therefore to be expected that reaction of a bis(arylsulphonyl)hydroxylamine with a sulphonyl chloride would give for steric reasons an *O*- rather than an *N*-derivative: in accord with this, reaction of *NN*-bis(*p*-tolylsulphonyl)hydroxylamine with toluene-*p*-sulphonyl chloride is found to give *NNO*-tris(*p*-tolylsulphonyl)hydroxylamine.

Konigs reported[4] that the reaction of fuming HNO_3 on benzenesulphinic acid gave the tris species, although he regarded it as a trisubstituted amine oxide: this observation we have confirmed, although we were unable to substantiate the claim of Hinsberg[5] to have obtained bis(phenylsulphonyl)hydroxylamine by the action of HNO_2 on benzenesulphonamide. In contrast to carboxylic acid amides, benzenesulphonamide is remarkably inert towards HNO_2, and under most reaction conditions is recovered unchanged: the only other product we identified was diphenyl disulphone, $(PhSO_2)_2$, which may have been produced by dimerisation of benzenesulphonyl radicals. Similarly we were unable to confirm the report of Piloty[6] that reaction of *N*-(phenylsulphonyl)hydroxylamine with $FeCl_3$ gives the bis derivative: we observed no reaction. It should be noted that the m.p. recorded by Piloty (110 °C) is substantially below ours (125 °C), as is also the value he reported for the tris derivative.

It appears that any nitrogen-containing oxidant will generate bis(arylsulphonyl)hydroxylamines from arenesulphinic acids, and that the bis compounds either do not react at all with oxidising agents or give the corresponding tris compounds, which represent a fairly deep potential trap in the energy hypersurface of this system. Thus a mild oxidising agent such as HNO_2 must be used if only the bis species is required: HNO_3 with an arenesulphinic acid yields the tris compound directly.

The reaction of toluene-*p*-sulphinic acid with *NN*-bis-(*p*-tolylsulphonyl)hydroxylamine in glacial acetic acid was reported by von Meyer[15] to give tris(*p*-tolylsulphonyl)amine, according to equation (4). We reinvestigated

$$p\text{-}MeC_6H_4SO_2H + (p\text{-}MeC_6H_4SO_2)_2NOH \longrightarrow (p\text{-}MeC_6H_4SO_2)_3N + H_2O \quad (4)$$

this reaction under von Meyer's conditions and find that, in air, copious evolution of nitrogen oxides occurs, giving toluene-*p*-sulphonic acid as the sole solid product. Under dry nitrogen, however, no nitrogen oxides were lost and the bis compound was recovered unchanged. It is possible that in von Meyer's experiment, part either of the arenesulphinic acid or of the bis compound was oxidised by the nitrogen oxides to tris(*p*-tolylsulphonyl)hydroxylamine: certainly the m.p. he quoted for material which he described as an amine, 184 °C, is very similar to that found in this work for the tri-substituted hydroxylamine, 183—184 °C.

Although all the bis(arylsulphonyl)hydroxylamines studied here are stable in dry air, only those having $X = p$-Me and p-Cl are stable to moisture. When $X = p$-F or H, moisture caused the evolution of nitrogen oxides, leaving RSO_3H and $(RSO_2)_2NOSO_2R$, while when $X = p$-MeO no nitrogen oxides were evolved and the sole product was a black tar. The rate of decomposition when X = F was so fast that accurate microanalysis was not possible: the fast decomposition when X = MeO may account for its rather poor microanalytical data. It is reasonable to suppose that the initial step in the decomposition is hydrolysis of an N–S bond: for hydrolysis of sulphonyl derivatives Hammett's ρ is positive,[28] and the σ_p constants suggest that the rates of hydrolysis should decrease in the order $Cl > F > H > Me > MeO$. However, the order of decomposition rates observed is $F > MeO > H > Me \simeq Cl$. For the tris derivatives the observed order is $F \simeq Cl \gg H \simeq Me \simeq MeO$, decomposition of the halogeno-species giving nitrogen oxides and the arenesulphonic acid.

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