Sulphur–Nitrogen Compounds. Part 2.[1] Reactions of (Arylsulphonyl)hydroxylamines with Nitrosyl Chloride, Nitrogen Monoxide, and Chlorine, and Some Related Reactions

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The compounds RSO_2NHOH, $(RSO_2)_2NOH$, and RSO_2NH_2 (R = Ph or p-MeC_6H_4) are all converted by nitrosyl chloride into RSO_2Cl, but $(RSO_2)_2NOSO_2R$ and $(RSO_2)_2NH$ are unaffected; RSO_2NHOH, $(RSO_2)_2NOH$, and $(RSO_2)_2NOSO_2R$ all initiate free-radical halogenation by dichlorine and dibromine, but not by di-iodine, of benzene and cyclohexane. Oxidation of $PhSO_2NHOH$ by a range of oxidants yields $PhSO_2Cl$, $PhSO_3H$, or $(PhSO_2)_2NOSO_2Ph$, but not $PhSO_2NO$. The compound p-$MeC_6H_4SO_2Na$ is converted by NOCl into p-$MeC_6H_4SO_2Cl$ rather than to p-$MeC_6H_4SO_2NO$; $(p$-$MeC_6H_4SO_2)_2NH$ is inert to a wide range of oxidants.

NN-BIS(ARYLSULPHONYL)HYDROXYLAMINES $(RSO_2)_2NOH$ are oxidised by a wide range of oxidising agents to yield nitrate and *NNO*-tris(arylsulphonyl)hydroxylamines,[1] $(RSO_2)_2NOSO_2R$: the route postulated for this conversion involves nitrosyl arenesulphinates, RSO_2NO, as intermediates. Such derivatives appear not to have been characterised, but possible routes to their formation include (*i*) reaction of sodium arenesulphinates with nitrosyl chloride, and (*ii*) oxidation of *N*-(arylsulphonyl)hydroxylamines under conditions which convert *N*-arylhydroxylamines to *C*-nitrosoarenes.[2] In this paper we report the results of some reactions of this type, together with those of some related reactions.

RESULTS AND DISCUSSION

Sodium toluene-*p*-sulphinate is converted almost quantitatively into toluene-*p*-sulphonyl chloride by excess of nitrosyl chloride [equation (1)]. A plausible

$$p\text{-}MeC_6H_4SO_2Na + 2NOCl \longrightarrow NaCl + p\text{-}MeC_6H_4SO_2Cl + 2NO \quad (1)$$

intermediate in this reaction is nitrosyl toluene-*p*-sulphinate, but with a 1 : 1 molar ratio of the reactants p-$MeC_6H_4SO_2Cl$ was again formed (46%), leaving unchanged p-$MeC_6H_4SO_2Na$; reaction of the sodium salt with the sulphonyl chloride to yield di-*p*-tolyl disulphone[3] is slow under these conditions. If p-$MeC_6H_4SO_2NO$ is an intermediate, it reacts further with NOCl at a rate greater than that of its formation. That no *NN*-bis(*p*-tolylsulphonyl)hydroxylamine is formed confirms that the corresponding reaction[1] with sodium nitrite–hydrochloric acid mixtures involves nitrous acid rather than NOCl. The products of the reactions of NOCl with a number of related sulphonyl amides and hydroxylamines are summarised in Table 1: $(RSO_2)_2NH$ and $(RSO_2)_2NOSO_2R$ (R = Ph or p-MeC_6H_4 throughout this paper) did not react, but the remainder were converted into RSO_2Cl. In none of its reactions did NOCl act as an oxidising agent to yield bis- or tris-(arylsulphonyl)hydroxylamines from simpler substrates (*cf.*[1] HNO_2 and HNO_3). The nitrogen-containing species attacked by NOCl contain either an $>$NOH or an $-NH_2$ fragment suggesting reaction *via* $>$N–O in the former case and *via* diazotisation in the latter.

Since nitrosyl chloride is slightly dissociated into chlorine and nitrogen monoxide, and since NO may be a primary product in some of its reactions with arylsulphonyl compounds, the corresponding reactions of chlorine and NO with arylsulphonyl compounds were investigated. The products of the nitrogen oxide reactions are summarised in Table 1. The principal product from the (arylsulphonyl)hydroxylamines was the corresponding arenesulphonic acid; toluene-*p*-sulphinic acid and its sodium salt were largely unchanged with no conversion into hydroxylamine derivatives as suggested by Konigs,[4] but a small quantity of the disulphone $(p$-$MeC_6H_4SO_2)_2$ was isolated from the reaction of the sulphinic acid; the imide $(p$-$MeC_6H_4SO_2)_2NH$ was unaffected by both NO and NO_2, as by NOCl.

Chlorine reacted with p-$MeC_6H_4SO_2Na$ to yield p-$MeC_6H_4SO_2Cl$ when in excess [equation (2)] and a

$$p\text{-}MeC_6H_4SO_2Na + Cl_2 \longrightarrow p\text{-}MeC_6H_4SO_2Cl + NaCl \quad (2)$$

mixture of toluene-*p*-sulphonyl chloride and unchanged sodium salt, but no disulphone, when in 1 : 2 molar ratio. (Arylsulphonyl)hydroxylamines, when treated with chlorine in benzene or cyclohexane, initiated ready halogenation of the solvent, as do a number of simple

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[1] Part 1 is regarded as J. D. Birchall and C. Glidewell, *J.C.S. Dalton*, 1977, 10.

[2] (*a*) O. Wichterle, V. Gregor, A. Dubanský, and V. Seidl, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1158; (*b*) C. S. Marvel and O. Kamm, *J. Amer. Chem. Soc.*, 1919, **41**, 276; (*c*) G. H. Coleman, C. M. McCloskey, and F. A. Stewart, *Org. Synth.*, 1955, Coll. vol. 3, 668; (*d*) T. Emery and J. B. Neilands, *J. Org. Chem.*, 1962, **27**, 1075; (*e*) E. Bamberger, *Ber.*, 1894, **27**, 1555; (*f*) O. Piloty and I. Ruff, *ibid.*, 1897, **30**, 1656.

[3] E. P. Kohler and M. B. MacDonald, *Amer. Chem. J.*, 1899, **22**, 219.

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

amines and amides (see Table 2). Control reactions showed no chlorination of the hydrocarbons, and the reactions in carbon tetrachloride showed that, in the absence of a substrate for radical attack, no net change occurred: only *N*-(phenylsulphonyl)hydroxylamine underwent reaction with chlorine, being partially converted into benzenesulphonyl chloride. The efficiency of the chlorination of benzene was generally much higher than that of cyclohexane: no nuclear chlorination of PhX (X = F, Cl, Br, or I) or of $SiPh_2H_2$ was observed.

TABLE 1

Products from reactions of arylsulphonyl species with excess of nitrosyl chloride or nitrogen monoxide

Substrate	Product (yield/%)	
	NOCl–Et_2O	NO–Et_2O–C_6H_6
p-$MeC_6H_4SO_2Na$	*p*-$MeC_6H_4SO_2Cl$ (97)	*p*-$MeC_6H_4SO_2Na$ (87) *p*-$MeC_6H_4SO_3H$ (6.3)
p-$MeC_6H_4SO_2H$	*p*-$MeC_6H_4SO_2Cl$ (93)	*p*-$MeC_6H_4SO_2H$ (70) (*p*-$MeC_6H_4SO_2)_2$ (1.5)*
p-$MeC_6H_4SO_3Na$	*p*-$MeC_6H_4SO_3Na$ (100)	
p-$MeC_6H_4SO_2NH_2$	*p*-$MeC_6H_4SO_2Cl$ (94)	
(*p*-$MeC_6H_4SO_2)_2NH$	*p*-$Me(C_6H_4SO_2)_2NH$ (100)	*p*-$(MeC_6H_4SO_2)_2NH$ (100)
$(PhSO_2)NHOH$	$PhSO_2Cl$ (85)	$PhSO_2NHOH$ (12) $PhSO_3H$ (57) $(PhSO_2)_2$ (trace)
$(PhSO_2)_2NOH$	$PhSO_2Cl$ (92)	$PhSO_3H$ (93)
(*p*-$MeC_6H_4SO_2)_2NOH$	*p*-$MeC_6H_4SO_2Cl$ (100)	*p*-$MeC_6H_4SO_3H$ (99)
$(PhSO_2)_2NOSO_2Ph$	$(PhSO_2)_2NOSO_2Ph$ (100)	
(*p*-$MeC_6H_4SO_2)_2NOSO_2C_6H_4Me$-*p*	(*p*-$MeC_6H_4SO_2)_2NOSO_2C_6H_4Me$-*p* (100)	*p*-$MeC_6H_4SO_3H$ (83)

* Identified by m.p. 209 °C (lit.,[12] 210—212 °C) and mass spectrum.

TABLE 2

Results of chlorination reactions

Substrate	Product (yield/%) from		
	Benzene	Cyclohexane	Carbon tetrachloride
p-$MeC_6H_4SO_2NH_2$	$C_6H_6Cl_6$ [a] (37)	$C_6H_6Cl_6$ (2.2)	S (88)
(*p*-$MeC_6H_4SO_2)_2NH$	$C_6H_6Cl_6$ (33)	$C_6H_6Cl_6$ (4.2)	S (81)
$PhCONH_2$	$C_6H_6Cl_6$ (10)	S (92) $C_6H_6Cl_6$ (trace)	S (88)
$MeCONH_2$	$C_6H_6Cl_6$ (17)	S (92)	S (92)
$MeCONMe_2$	$C_6H_6Cl_6$ (4.3)	S (71)	S (86)
$MeCSNH_2$	S [b] (80)	S (73)	S (80)
$PhSO_2NHOH$	$C_6H_6Cl_6$ (4.3)	$C_6H_6Cl_6$ (1.5)	S (35) $PhSO_2Cl$ (46)
(*p*-$MeC_6H_4SO_2)_2NOH$	$C_6H_6Cl_6$ (35)	$C_6H_6Cl_6$ (5.0)	S (97)
(*p*-$MeC_6H_4SO_2)_2NOSO_2C_6H_4Me$-*p*	$C_6H_6Cl_6$ (21)	S (50)	S (98)
Et_3N	$C_6H_6Cl_6$ (3.5)	$[NHEt_3]Cl$ (93)	$[NHEt_3]Cl$ (88)
$[NMe_4]I$	S (86)	S (92)	S (94)

[a] The $C_6H_6Cl_6$ formed was always a mixture of stereoisomers. [b] S denotes nitrogen compound recovered unchanged.

No chlorination of diethyl ether was observed in the presence of $PhSO_2NHOH$ or $(RSO_2)_2NOSO_2R$, but in the presence of *p*-$MeC_6H_4SO_2NH_2$ 1,2-dichloroethyl ethyl ether was formed in *ca.* 70% yield although the usual radical-induced chlorination yields a succession of products.[5] In contrast to the amides $PhCONH_2$, $MeCONH_2$, and $MeCONMe_2$, thioacetamide $MeCSNH_2$ initiated no chlorination.

Reactions conducted in darkness gave the same products as those in normal daylight, excluding photochemical initiation. When bromine was employed in reactions with (arylsulphonyl)hydroxylamines, in benzene or cyclohexane, the yields of halogenated hydrocarbon were very much lower than from the chlorination reactions: no reaction whatever was observed with iodine, nor was any radical arylation observed when $(RSO_2)_2NOH$ was treated with bromine in the presence of a mixture of *p*-chlorobenzoic acid and nitrobenzene. The $C_6H_6Cl_6$ formed in the chlorination reactions of benzene is a mixture of stereoisomers of which α and γ (major components) and β and δ (minor components) were identified by high pressure liquid chromatography (h.p.l.c.); when the initiator was $(RSO_2)_2NOH$, $(RSO_2)_2NOSO_2R$ also was identified in the product, but RSO_2Cl was absent.

The reactions with benzene and cyclohexane indicate formation of halogen atoms, $X^\bullet$, in solution, which react with benzene by addition and with cyclohexane *via* the chain process [equations (3)—(5)]. Since both triethyl- and triphenyl-amine, but not the tetramethylammonium cation, initiate this addition halogenation of benzene, the minimum requirement for initiation appears to be an unshared electron pair on nitrogen; by analogy with the R_3N–CCl_4 reaction,[6] a plausible initiation process,

$$X^\bullet + C_6H_{12} \longrightarrow HX + C_6H_{11}^\bullet \qquad (3)$$

$$C_6H_{11}^\bullet + X_2 \longrightarrow C_6H_{11}X + X^\bullet \qquad (4)$$

$$X^\bullet + C_6H_{11}X \longrightarrow HX + C_6H_{10}X^\bullet, \textit{ etc.} \qquad (5)$$

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[5] G. E. Hall and F. M. Ubertini, *J. Org. Chem.*, 1960, **15**, 715.

[6] J. R. Lindsay-Smith and Z. A. Malik, *J. Chem. Soc.* (*B*), 1970, 920.

consistent both with these observations, and with the order of reactivity of the elemental halogens ($Cl_2 > Br_2 > I_2$) towards $R^1R^2R^3N$ is (6), possibly followed for $(RSO_2)_2NOZ$ ($Z = H$ or SO_2R) by equations (7)—(9)

$$R^1R^2R^3N + X_2 \rightleftharpoons [R^1R^2R^3N]^{+\cdot} + X^\cdot + X^- \tag{6}$$

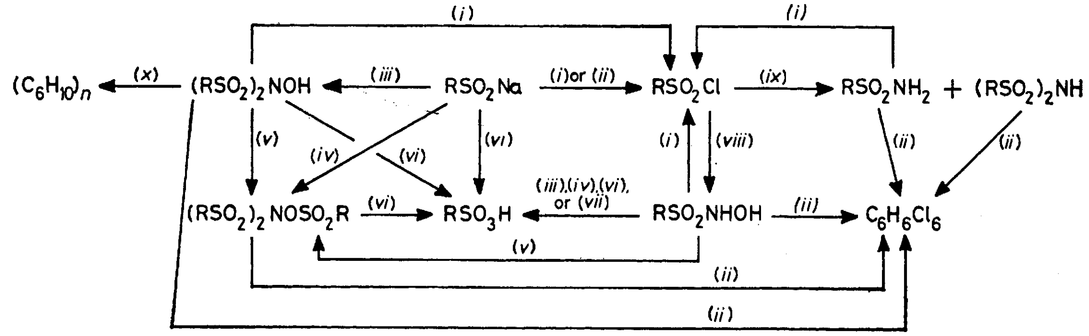
$$[(RSO_2)_2NOZ]^{+\cdot} + X^- \longrightarrow (RSO_2)_2NO^\cdot + ZX \tag{7}$$

$$(RSO_2)_2NO^\cdot \longrightarrow Y^\cdot \tag{8}$$

$$Y^\cdot + X_2 \longrightarrow YX + X^\cdot \tag{9}$$

(R = aryl) where $Y^\cdot$ is a radical which may be $(RSO_2)_2NO^\cdot$, or more plausibly $RSO_2^\cdot$. Termination of radical processes, as in carbon tetrachloride, may be by reversal of reactions (6).

A number of reagents [2] convert *N*-arylhydroxylamines RNHOH into *C*-nitrosoarenes RNO, but none of these reagents converts *N*-(phenylsulphonyl)hydroxylamine to nitrosyl benzenesulphinate, $PhSO_2NO$. The reaction of $PhSO_2NHOH$ with chlorine is described above, and the products of its reactions with NOCl and NO are noted in Table 1. Aqueous oxidants yield benzenesulphonic acid, although the hydrolysis of $PhSO_2NHOH$ alone is slow. Lead(IV) oxide yields $(PhSO_2)_2NOSO_2Ph$, but silver(I,III), manganese(IV), and mercury(II) oxides do not react. These results contrast markedly with those for the oxidation both of *N*-arylhydroxylamines, and of species $(RSO_2)_2NOH$ [1] which are converted into $(RSO_2)_2NOSO_2R$ by AgO, MnO_2 (although not by HgO), and nitric acid, but which are inert to most other oxidants. Peroxomonosulphuric acid [7] did not oxidise toluene-*p*-sulphonamide to the *S*-nitroso-compound, nor did p-$MeC_6H_4SO_2Cl$ react with silver nitrite. A range of oxidants was without effect on bis(sulphonyl)amines, $(RSO_2)_2NH$ (see Experimental section).



SCHEME Reactions of arylsulphonyl compounds. R = Ph or p-MeC_6H_4. Reagents: (*i*) NOCl–Et_2O, (*ii*) Cl_2–C_6H_6, (*iii*) HNO_2(aq),[1] (*iv*) HNO_3,[1] (*v*) PbO_2–C_6H_6,[1] (*vi*) NO–Et_2O–C_6H_6, (*vii*) aqueous oxidants (see Experimental section), (*viii*) NH_2OH, (*ix*) NH_3 (g), and (*x*) PbO_2–C_6H_{10}

The intial step in the oxidation of $(RSO_2)_2NOH$ by a range of reagents was postulated [1] to be loss of a hydrogen atom to yield the radical $(RSO_2)_2NO^\cdot$, part of which dissociates to give $RSO_2^\cdot$ (and RSO_2NO), subsequent cross-combination of the radicals yielding the product $(RSO_2)_2NOSO_2R$. The occurrence of the first step is supported by the failure of the corresponding bis(arylsulphonyl)amines $(RSO_2)_2NH$ to undergo oxidation by any of the reagents, except chlorine, which oxidise $(RSO_2)_2NOH$. Also suggestive of the intermediacy of radicals is the observation that, in cyclohexene, conversion of $(RSO_2)_2NOH$ into $(RSO_2)_2NOSO_2R$ by PbO_2 is suppressed in favour of oligomerisation of the cyclohexene. The reactions of arenesulphonyl species described here and previously [1] are summarised in the Scheme.

EXPERIMENTAL

Starting materials have been described.[1] Nitrosyl chloride, nitrogen monoxide, and chlorine were commercial products and were used as received. Reactions involving these gases were carried out during 24 h at 0 °C; reactions with NO were conducted in an atmosphere of dry dinitrogen. Literature methods were used for the preparation of $(MeSO_2)_2NH$,[8] $(p$-$XC_6H_4SO_2)_2NH$ (X = H,[9] Me,[9] and Cl [10]), $(ClSO_2)_2NH$,[11] and $(p$-$MeC_6H_4SO_2)_2$.[12] High-pressure liquid chromatography (h.p.l.c.) was performed using a Pye–Unicam model LC3, with the u.v. detector set at 240 nm, and using 1% dioxan in hexane as solvent.

Preparation of NN-*Bis(piperidinosulphonyl)amine*.—Piperidine (6.80 g, 0.081 mol) was added slowly to a stirred solution of iminobis(sulphonyl chloride) (4.28 g, 0.020 mol) in benzene (75 cm^3). The solution was refluxed during 15 min, cooled, and filtered, and the solvent was evaporated. The crude product was heated with water (50 cm^3) on a steam-bath, filtered, and dried, yield 70%, m.p. 139—140 °C (Found: C, 38.3; H, 7.00; N, 13.1. $C_{10}H_{21}NO_4S_2$ requires C, 38.6; H, 6.80; N, 13.5%). The ^1H n.m.r. spectrum had peaks at δ 1.28 (m, 12 H), 3.28 (t, 8 H), and 7.18 (s, 1 H) p.p.m.

Reaction of Nitrosyl Chloride with Sodium Toluene-p-*sulphinate*.—(*a*) A solution of nitrosyl chloride (0.89 g, 13.7 mmol) in diethyl ether (100 cm^3) was added during 0.5 h to a suspension of sodium toluene-*p*-sulphinate (2.42 g, 13.7 mmol); after 24 h the mixture was filtered. The residue contained sodium nitrate, nitrite, and chloride, and unchanged p-$MeC_6H_4SO_2Na$, which was characterised by

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[7] C. K. Ingold, *J. Chem. Soc.*, 1924, **125**, 87.

[8] B. Helferich and H. Flechsig, *Ber.*, 1942, **75**, 532.

[9] N. N. Dykhanov, *Zhur. obshchei Khim.*, 1959, **29**, 3602.

[10] F. Runge, H. Engelbrecht, and G. Preusser, *Ber.*, 1953, **86**, 1571.

[11] R. Appel, M. Becke-Goehring, M. Eisenhauser, and J. Hautenstein, *Ber.*, 1962, **95**, 625.

[12] T. P. Hilditch, *J. Chem. Soc.*, 1908, **93**, 1524.

reaction with aqueous nitrous acid[1] to yield *NN*-bis(*p*-tolylsulphonyl)hydroxylamine (1.02 g, 3.0 mmol, 43.8%, m.p. 123 °C). Evaporation of the filtrate yielded toluene-*p*-sulphonyl chloride (1.20 g, 6.3 mmol, 46.0%), which after recrystallisation from diethyl ether had m.p. and mixed m.p. 70 °C.

(*b*) Sodium toluene-*p*-sulphinate (1.78 g, 0.01 mol) in diethyl ether (150 cm^3) was treated with an excess of gaseous NOCl. Removal of the volatiles gave p-MeC$_6$H$_4$SO$_2$Cl (1.85 g, 9.7 mmol, 97%).

Reaction of NN-*Bis*(p-*tolylsulphonyl*)*hydroxylamine with Nitrosyl Chloride*.—(*a*) A solution of NOCl (0.159 g, 2.4 mmol) in diethyl ether (100 cm^3) was added to a suspension of *NN*-bis(*p*-tolylsulphonyl)hydroxylamine (0.82 g, 2.4 mmol) in diethyl ether (100 cm^3): after stirring for 24 h the mixture was evaporated. Extraction of the solid residue with diethyl ether (5 × 100 cm^3) left unchanged (p-MeC$_6$H$_4$SO$_2$)$_2$NOH (0.31 g, 0.91 mmol, 38%): evaporation of the ether extracts gave p-MeC$_6$H$_4$SO$_2$Cl (0.39 g, 2.0 mmol, 42%).

(*b*) With an excess of gaseous NOCl, (p-MeC$_6$H$_4$SO$_2$)$_2$NOH (1.02 g, 3.0 mmol) yielded p-MeC$_6$H$_4$SO$_2$Cl (1.14 g, 6.0 mmol, 100%).

The products of the reactions of other arylsulphonyl compounds with an excess of gaseous NOCl (in diethyl ether or benzene) are summarised in Table 1.

Reactions with Nitrogen Monoxide.—Typically, the substrate was dissolved or suspended in diethyl ether or benzene and an excess of the gas was bubbled in, the apparatus being flushed with dry dinitrogen meanwhile. Subsequent removal of excess of NO with dinitrogen, followed by evaporation of the volatiles, afforded the products (Table 1).

Oxidations of N-(*Phenylsulphonyl*)*hydroxylamine*.—(a) *Nitrosyl chloride*. Nitrosyl chloride (0.159 g, 2.4 mmol) and *N*-(phenylsulphonyl)hydroxylamine (0.42 g, 2.4 mmol) were mixed in diethyl ether (100 cm^3). Oxides of nitrogen were evolved; after 24 h the mixture was evaporated to yield benzenesulphonyl chloride (0.42 g, 2.4 mmol, 100%).

(b) *Chlorine*.[2a] A solution of chlorine (2.0 mmol) in carbon tetrachloride (50 cm^3) was added to a solution of PhSO$_2$NHOH (0.84 g, 4.8 mmol) in the same solvent (50 cm^3). After 24 h, removal of the solvent yielded PhSO$_2$Cl (0.42 g, 2.2 mmol, 46%) and unchanged starting material (0.30 g, 1.7 mmol, 35%); use of excess of chlorine with diethyl ether as solvent gave PhSO$_2$Cl (90%). No chloroethyl ethers were detected.

(c) *Nitrogen monoxide*. *N*-(Phenylsulphonyl)hydroxylamine (1.73 g, 0.01 mol) in benzene (100 cm^3) was treated with an excess of gaseous nitrogen monoxide. After evaporation of the volatiles, benzene extraction of the residue gave unchanged PhSO$_2$NHOH (0.20 g, 1.2 mmol, 12%) leaving benzenesulphonic acid (0.90 g, 5.7 mmol, 57%) contaminated with a small quantity of diphenyl disulphone, identified mass spectrometrically.

(d) *Nitrous acid*.[2b] To a stirred aqueous solution containing PhSO$_2$NHOH (1.73 g, 0.01 mol) and sodium nitrite (0.69 g, 0.01 mol) was added concentrated HCl (3 cm^3). Subsequent filtration and evaporation yielded PhSO$_3$H (1.30 g, 8.2 mmol, 82%).

(e) *Nitric acid*.[1] *N*-(Phenylsulphonyl)hydroxylamine (1.73 g, 0.01 mol) was stirred in glacial acetic acid (100 cm^3) with an excess of concentrated HNO$_3$. Oxides of nitrogen were evolved and, after removal of the volatiles, PhSO$_3$H was isolated (76%).

(f) *Acid sodium dichromate*.[2c] *N*-(Phenylsulphonyl)hydroxylamine (1.73 g, 0.01 mol) was dissolved in 98% H$_2$SO$_4$ (2 cm^3): ice-cold aqueous sodium dichromate (0.57 g, 2.2 mmol in 25 cm^3) was added and the solution was stirred. The mixture was extracted with benzene (4 × 25 cm^3): evaporation of the benzene extracts yielded PhSO$_3$H (1.22 g, 7.7 mmol, 77%).

(g) *Periodic acid*[2d] *and sodium hypochlorite*.[2e] Reactions as in (f), with excess of 55% aqueous periodic acid, or sodium hypochlorite solution, gave PhSO$_3$H (76 and 68% respectively).

(h) *Metal oxides*.[1] *N*-(Phenylsulphonyl)hydroxylamine (1.73 g, 0.01 mol) was stirred at room temperature during 24 h with an excess of lead(IV) oxide, suspended in benzene. After centrifugation, evaporation of the solvent yielded *NNO*-tris(phenylsulphonyl)hydroxylamine (0.77 g, 1.70 mmol, 51%; m.p. and mixed m.p.[1] 88—90 °C). With mercury(II),[2f] silver(I,III), and manganese(IV) oxides under similar conditions, no oxidation of PhSO$_2$NHOH occurred.

Reaction of NN-*Bis*(p-*tolylsulphonyl*)*hydroxylamine with Halogens*.—(*a*) *With Chlorine*. *NN*-Bis(*p*-tolylsulphonyl)hydroxylamine (1.70 g, 5.0 mmol) was dissolved in benzene (100 cm^3) and an excess of chlorine gas was bubbled in. Subsequent removal of the volatiles yielded a pale yellow solid, m.p. 90—95 °C, whose mass spectrum contained ion clusters up to m/e 288 $[\mathrm{C_6H_6Cl_6}]^+$ and 330 $[\mathrm{C_6H_6Cl_5C_6H_5}]^+$. The mass of the ion at m/e 288 was 287.8584 a.u.; $[\mathrm{C_6H_6{}^{35}Cl_6}]^+$ requires 287.8601 a.u. Microanalysis: found C, 26.7; H, 2.40. C$_6$H$_6$Cl$_6$ requires C, 25.0; H, 1.40%. H.p.l.c. revealed eight components: fractional crystallisation[13] of the crude mixture afforded authentic samples of the α, β, γ, and δ isomers of C$_6$H$_6$Cl$_6$, enabling four components to be identified. Compounds RSO$_2$Cl were absent.

A similar reaction in cyclohexane gave a similar solid, m.p. 88—96 °C. From an analogous reaction in carbon tetrachloride, the starting material was recovered unchanged. Identical results were obtained for reactions conducted in the presence or in the absence of light.

(*b*) *With bromine*. (*i*) Bromine (48.0 g, 0.3 mol) was added during 20 min to a solution of (p-MeC$_6$H$_4$SO$_2$)$_2$NOH (0.34 g, 1.0 mmol) in benzene (7.8 g, 0.1 mol). After removal of all the volatiles, the solid product (1.5 g, m.p. 95—105 °C) exhibited ions up to $[\mathrm{C_6H_4Br_5}]^+$ in its mass spectrum.

(*ii*) Bromine (192 g, 1.2 mol) was added slowly to a solution of (p-MeC$_6$H$_4$SO$_2$)$_2$NOH (0.34 g, 1.0 mmol) in cyclohexane (8.4 g, 0.1 mol), and the mixture was stirred overnight. Removal of the volatiles yielded an identical solid product (1.1 g).

(*c*) *With iodine*. Reaction with iodine in benzene gave only unchanged starting materials.

Reactions of Other Nitrogenous Compounds with Chlorine.—The nitrogenous initiator (0.01 mol) was dissolved or suspended in the substrate as solvent (1.0 mol) at 0 °C, and chlorine gas (1.0 mol) was slowly introduced in the absence of light. After removal of all the volatiles, the products remaining were identified by microanalysis and mass spectrometry (Table 2).

Reaction of Diethyl Ether with p-MeC$_6$H$_4$SO$_2$NH$_2$ *and* Cl$_2$.—Chlorination as above yielded 1,2-dichloroethyl ethyl ether (70%) [^{1}H n.m.r.: δ 1.28 (t, 3 H), 3.50 (q, 2 H), 3.75 (d, 2 H), and 5.56 (t, 1 H) p.p.m.], identified by comparison (^{1}H n.m.r., mass spectrum, and g.l.c.) with an authentic sample.[14]

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Attempted Oxidation of Bis(sulphonyl)amines.—No oxidation was observed during 1 week, for the following: bis(*p*-tolylsulphonyl)amine with H_2O_2–$Na_2[WO_4]$(aq),[15] *m*-$ClC_6H_4CO_2H$–Et_2O,[16] $K[MnO_4]$–Me_2CO, PbO_2–Me_2CO, Ce^{3+}–H_2O_2(aq),[15] H_2O_2–MeOH,[15a] and Fe^{2+}–H_2O_2(aq);[15a] bis(phenylsulphonyl)amine with H_2O_2–$Na_2[WO_4]$(aq) and *m*-$ClC_6H_4CO_3H$–Et_2O; bis(*p*-chlorophenylsulphonyl)amine with H_2O_2–$Na_2[WO_4]$(aq); bis(piperidinosulphonyl)amine with H_2O_2–$Na_2[WO_4]$(aq), *m*-$ClC_6H_4CO_3H$–Et_2O, and PbO_2–Me_2CO; and bis(methylsulphonyl)amine with H_2O_2–Na_2-$[WO_4]$(aq).

Reaction of Benzenesulphonamide with Peroxomonosulphuric Acid.[7]—Equimolar quantities (0.05 mol) of benzenesulphonamide and the freshly prepared peroxoacid were stirred together at 0 °C during 1 h. The mixture was filtered and the product was washed and dried, affording unchanged $PhSO_2NH_2$ (90%).

*Reaction of Sodium Toluene-*p*-sulphinate with Chlorine.*—Sodium toluene-*p*-sulphinate (0.87 g, 4.9 mmol) was stirred during 24 h with chlorine (2.43 mmol) in carbon tetrachloride (50 cm^3). After filtration, the residue was dried and treated with excess of aqueous HNO_2; $(p\text{-}MeC_6H_4SO_2)_2$-NOH (0.35 g, 1.03 mmol, 42%) was extracted with benzene. The original filtrate was evaporated to yield *p*-$MeC_6H_4SO_2Cl$ (0.45 g, 2.36 mmol, 48%). With excess of chlorine gas, an almost quantitative yield of *p*-$MeC_6H_4SO_2Cl$ was obtained. When di-*p*-tolyl disulphone (1.50 g, 4.84 mmol) was treated in benzene solution with an excess of chlorine gas, *p*-MeC_6H_4-SO_2Cl (1.80 g, 9.45 mol, 97%) was obtained after removal of the volatiles.

*Reaction of Toluene-*p*-sulphonyl Chloride with Silver Nitrite.*—Toluene-*p*-sulphonyl chloride (2.0 g, 10.5 mmol) was stirred during 24 h with an excess of dry silver nitrite, suspended in benzene (150 cm^3). Filtration and removal of the solvent yielded an oil (1.8 g, 9.4 mmol, 90%) which crystallised after 3 d at 0 °C; after recrystallisation from diethyl ether the m.p. and mixed m.p. with *p*-$MeC_6H_4SO_2Cl$ were 68—69 °C.

Reaction of NN-*Bis(*p*-tolylsulphonyl)hydroxylamine with Lead*(IV) *Oxide in Cyclohexene.*—The hydroxylamine (1.7 g, 5.0 mmol) was stirred in cyclohexene (150 cm^3, 1.48 mol) with an excess of lead(IV) oxide during 24 h. The mixture was centrifuged and the solvent was evaporated. The oil remaining was extracted with acetone: evaporation of the extracts yielded $(p\text{-}MeC_6H_4SO_2)_2NOH$ (1.4 g, 4.1 mmol, 82%) but no *NNO*-tris(*p*-tolylsulphonyl)hydroxylamine. The residual oil contained no aromatic protons (n.m.r.), no RSO_2 fragments (mass spectrum), and was scarcely volatile in an oil-pump vacuum. No such hydrocarbon was formed in a control reaction.

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