The Reaction of *N*-Alkylhydroxamic Acids with Sulphinyl Chlorides

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The reaction of several *N*-methylhydroxamic acids with methane- and benzene-sulphinyl chloride is shown to give an isolatable *O*-sulphinylated intermediate (**IV**) below 0 °C. The intermediates decompose at ambient temperatures with simultaneous N–O and S–O bond fission to give the isomeric *N*-acyl-*N*-methylsulphonamide (**V**) and *N*-methyl-*O*-sulphonylhydroxamic acid (**VI**) by in-cage and free pair radical recombination. ^{1}H and ^{13}C n.m.r. spectra show strong polarisations in both sulphonamide (**V**) and *O*-sulphonylhydroxamic acid (**VI**), indicating radical cage mechanisms. In addition, a strong e.s.r. signal was observed due to the *N*-acyl-*N*-methylnitroxyl radical (**X**).

In earlier work[1] we have shown that the reaction between dialkylhydroxylamines and sulphinyl chlorides to give sulphonamides proceeds by the intermediate formation of the *O*-sulphinylated hydroxylamine, which dissociates homolytically above 0 °C. Recombination in the radical cage produces the sulphonamide, but a significant proportion of the reaction leads to imine and sulphinic acid. Oximes react similarly[2] to give high yields of the sulphonylimine, and Engberts[3] has shown that alkyl *N*-hydroxycarbamates react with t-butylsulphinyl chloride to give the corresponding sulphonylcarbamates (**I**) and the t-butylsulphonyloxycarboximidate (**II**) and products formed from escaped radicals (Scheme 1). The sulphinyl intermediate (**III**) was not isolated but ^{1}H CIDNP effects showed that both (**I**) and (**II**) were formed by in-cage recombination involving the ambident amidyl radical. Subsequently Heesing[4] found that *N*-phenylhydroxamic acids react with sulphinyl chlorides at −70 °C to give the *N*-acylsulphonamides by a radical pair mechanism, together with anilide and *o*- and *p*-sulphonylbenzanilides.

In this paper we investigate the mechanism of the reaction between *N*-methylbenzohydroxamic acids and sulphinyl chlorides.

Results and Discussion

The *O*-sulphinylated hydroxamic acid (**IV**) was obtained as a solid by treatment of the *N*-methylbenzohydroxamic acid with methane- or benzene-sulphinyl chloride in dichloromethane in the presence of 1 equiv. of triethylamine or pyridine. These intermediates (**IV**) were characterised by ^{1}H and ^{13}C n.m.r. spectroscopy (Table 1).

The rearrangement, carried out in dichloromethane at room temperature, gave a mixture of products in addition to the anticipated *N*-methyl-*N*-acylsulphonamide (**V**). This was characterised by elemental analysis and mass spectroscopy (Tables 1 and 4) and was differentiated from the isomer (**IV**) by n.m.r. spectroscopy. In particular the ^{13}C absorption of the *N*-methyl group of (**V**) (δ *ca.* 35.7 p.p.m.) is to high field of the corresponding *N*-methyl resonance in (**IV**) (δ *ca.* 42 p.p.m.). The ^{1}H absorption of the *N*-methyl group is also to high field for (**V**) (δ *ca.* 3.3) compared with δ *ca.* 3.6 for (**IV**). The sulphonyl group [of (**V**)] shows characteristic i.r. absorptions at *ca.* 1 350 and *ca.* 1 160 cm^{-1}.

In addition to the amide (**VII**), the *O*-sulphonylhydroxamic acid (**VI**) was isolated as a major product. This was also characterised by elemental analysis and mass spectroscopy (Tables 1 and 4), and by n.m.r. spectroscopy. From Table 1 it is seen that the ^{13}C absorption for the *N*-methyl carbon atom is δ 40—42, *i.e.* close to the corresponding resonance of the starting material (**IV**) (δ 41—42). In the rearrangements of the benzenesulphinyl compounds (**IVb** and **d**) a further product was isolated, in *ca.* 20% yield. This was shown to be phenyl benzenethiosulphonate (**VIII**) characterised by independent synthesis and spectra (see Experimental section). The quantitative composition of the reaction mixture was determined by medium-pressure liquid chromatography with the results given in Table 2.

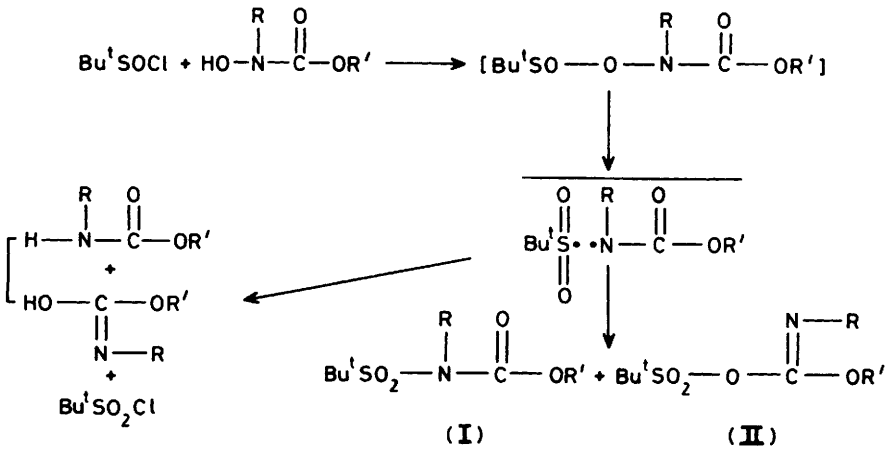
A product analogous to (**VIII**) was not isolated in the reactions of the methanesulphinyl compounds but the presence of methanesulphonyl chloride was detected by ^{1}H and ^{13}C n.m.r. spectroscopy (resonances at δ_H 3.66 and δ_C 52.6 p.p.m.).

The results given in Table 2 show that 97—100% of the amide group is incorporated in (**V**)—(**VII**) and therefore the reaction is essentially quantitative. It is noted that the yield of sulphonamide (**V**) is *ca.* 50% for the methanesulphonyl compounds and *ca.* 25% for the benzenesulphonyl compounds.

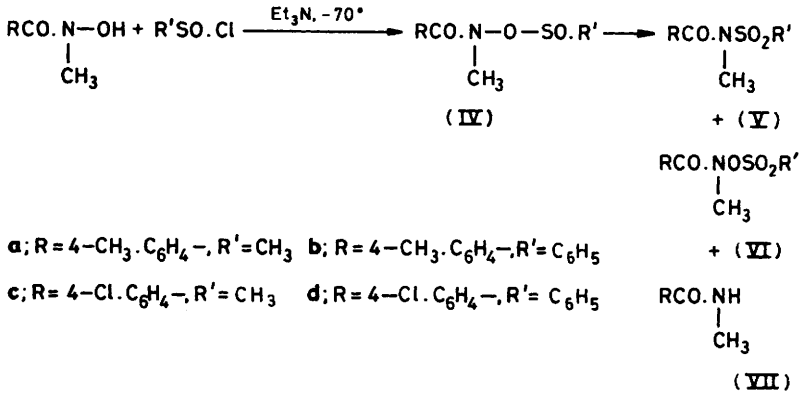
The Reaction Mechanism.—The sulphonamides (**V**) are obviously formed by a molecular rearrangement, but the mode of formation of (**VI**) is by no means clear. In the reactions of (**IVb** and **d**) this is a major product.

An important observation is the detection of a persistent radical in the e.s.r. spectrum of the reaction mixture (see Figure 1), with *g* 2.0068, a^N 7.37 and a^{N-CH_3} 8.10 G, identified as the acylnitroxyl radical. This is presumably formed by the homolysis of the S–O bond.

By analogy with our previous work on sulphinylated *N*-dialkylhydroxylamines,[1] the sulphonamide (**V**) may arise from N–O fission. Combination of sulphonyl radicals and acylnitroxide radicals could give rise to the *O*-sulphonylhydroxamic acid (**VI**). The amidyl radical could give rise to amide (**VII**), as observed in the homolytic rearrangement of thiocarbamoylated hydroxamic acids,[5] and the sulphinyl radical is known to give (**VIII**).[6] Direct evidence for these proposals was obtained from the enhanced polarisations observed in both the ^{1}H and ^{13}C n.m.r. spectra when the reaction was carried out rapidly at elevated temperatures in the probe of an n.m.r. spectrometer. The ^{13}C CIDNP spectrum of the reaction products from (**IVd**) shows a large number of polarisations, 10 of which can be



Scheme 1.



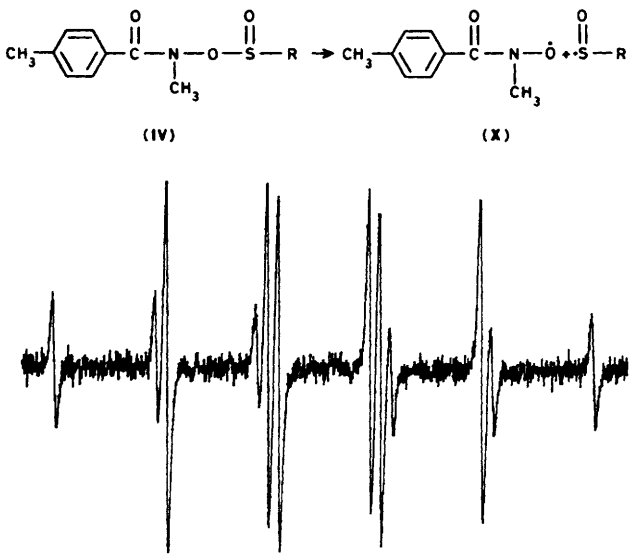
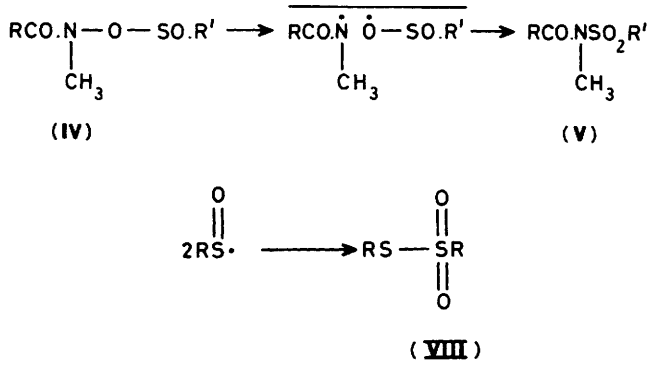


Figure 1. E.s.r. spectrum of the thermolysis of 4-$CH_3C_6H_4$-$CONCH_3OSOCH_3$ (**IVa**) at 25 °C



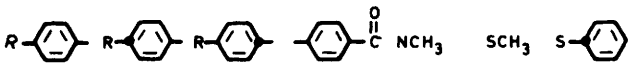
assigned using the spectroscopic data given in Table 1. These correspond to C-1 of the amido group of compound (**Vd**) (δ 131.10 p.p.m.), and (**VId**) (δ 130.83 p.p.m.), the carbonyl carbon atoms of (**Vd**) (δ 170.55 p.p.m.), (**VId**) (δ 170.11 p.p.m.), and (**VIIc**) (δ 167.40 p.p.m.), the *N*-methyl carbon atom of (**Vd**) (δ 35.29 p.p.m.), (**VId**) (δ 40.06 p.p.m.), and (**VIIc**) (δ 26.94 p.p.m.) and C-1 of the benzenesulphonyl group (δ 138.15 p.p.m.) in (**Vd**) and (**VId**) (δ 133.58 p.p.m.) (Figure 2).

These polarisations, shown qualitatively in Table 3, may be analysed by the sign equation (1) developed by Closs and Kaptein[7] (where the symbols have their usual meaning) in the following way. For a singlet precursor μ is negative, and positive

$$\Gamma_{ne} = \mu\varepsilon\Delta g_i\, a_i \qquad (1)$$

for a triplet precursor (F pair), ε is positive for in-cage recombination and negative for reaction due to escaped radicals, Δg is the difference in g values of the two radicals involved, and a_i is the sign of the hyperfine splitting constant of the nucleus observed. The g value for the benzamidyl radical is 2.0053,[8] and the values for the methane- and benzene-sulphonyl radicals are 2.0049 and 2.0046 respectively.[9] The hyperfine

Table 1. ^{13}C and ^{1}H n.m.r., i.r, and mass spectral data for *N*-methyl-*O*-sulphinylated hydroxamic acids (**IVa—d**), *N*-acyl-*N*-methylsulphonamides (**Va—d**), *N*-methyl-*O*-sulphonylhydroxamic acids (**VIa—d**), and *N*-methylbenzamides (**VIIIa,c**)

	$\delta_C(CDCl_3)^{a,b}$							$\delta_H(CDCl_3)^c$					
											C=O	SO_2	
											$\nu_{max.}/cm^{-1}$		
Compound											*m/z*		
(IVa)	21.38	141.72	129.37	171.48	42.30	40.84		2.36	3.60	2.67			
(IVb)	21.59	141.78	129.37	171.87	41.59		133.32	2.36	3.59				
(IVc)		138.94	130.12	171.52	41.92	40.90			3.64	2.67			
(IVd)		138.79	130.60	171.82	42.10		132.85		3.66				
(Va)	21.56	143.10	130.92	172.67	35.90	40.90		2.44	3.31	3.39	1 691	1 350 1 159	227
(Vb)	21.57	142.86	131.51	171.61	35.75		138.19	2.36	3.32		1 690	1 352 1 160	289 247.5
(Vc)		138.78	132.20	171.19	35.72	40.97			3.32	3.40			309.5
(Vd)		138.42	131.10	170.55	35.29		138.15		3.31				
(VIa)	21.57	142.83	130.16	171.47	42.47	37.66		2.40	3.52	3.05	1 699	1 375 1 185	243
(VIb)	21.48	142.04	129.43	171.43	40.90		133.68	2.37	3.52		1 690	1 381 1 195	305
(VIc)		138.50	130.87	170.17	42.01	38.11			3.59	3.12			263.5
(VId)		137.62	130.83	170.11	40.06		133.58		3.58				325.5
(VIIa)	21.39	141.50	131.68	168.19	26.75			2.36	2.94		1 634		
(VIIc)		137.59	132.95	167.40	26.94				3.04		1 633		

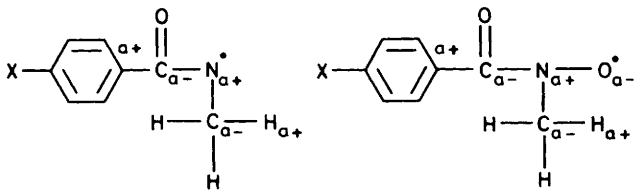
[a] 50.3 MHz (Fourier transform) ^{13}C shifts relative to internal Me_4Si at 25 °C. [b] Control experiment with (**Va**) showed no significant effect of temperature on chemical shifts. [c] 100 MHz (continuous wave) ^{1}H shifts relative to internal Me_4Si.

$$\Gamma_{ne} = \mu\varepsilon\Delta g_i a_i$$

^{13}C	Γ_{ne}* (**Vd**)[ε(+)]	Γ_{ne}* (**VId**)[ε(+)]	Γ_{ne}* (**VIIc**)[ε(−)]
Ar(C-1)	(−) = (−)(+)(+)(+)	(+) = (+)(+)(+)(+)	not observed
C=O	(+) = (−)(+)(+)(−)	(−) = (+)(+)(+)(−)	(−) = (−)(−)(+)(−)
NCH_3	(+) = (−)(+)(+)(−)	(−) = (+)(+)(+)(−)	(−) = (−)(−)(+)(−)
$ArSO_2$(C-1)	(+) = (−)(+)(−)(+)	(−) = (+)(+)(−)(+)	
^{1}H	Γ_{ne} (**Vd**)[ε(+)]	Γ_{ne} (**VId**)[ε(+)]	Γ_{ne} (**VIIc**)[ε(−)]
NCH_3	(−) = (−)(+)(+)(+)	(+) = (+)(+)(+)(+)	(+) = (−)(−)(+)(+)

Scheme 2. * $\Gamma_{ne}(+)$ = Enhanced absorption (A); (−) = enhanced emission (E).

splitting constants for the amidyl radical have been computed by the INDO method[5] and are as shown in (**IX**).



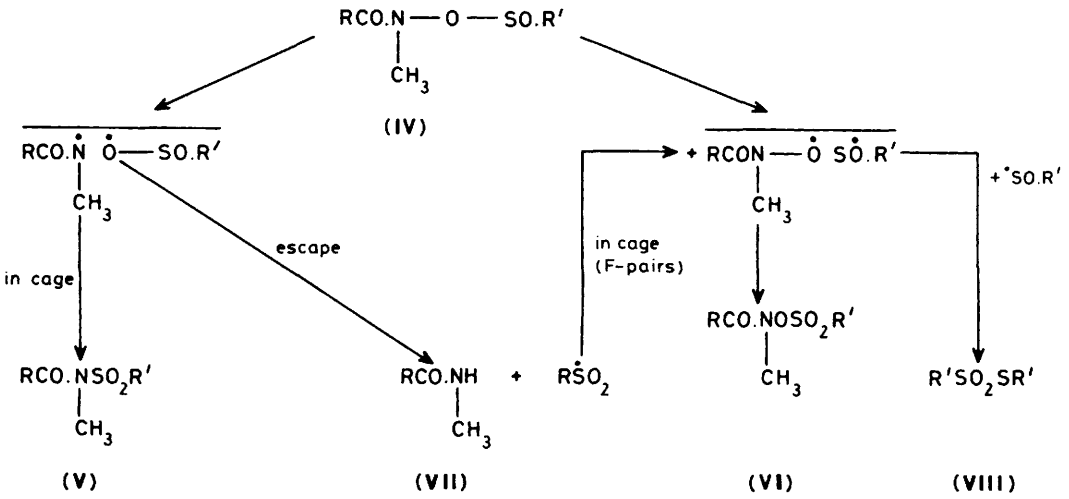
(**IX**) (**X**)

From previous work in the oxime series[2] a positive value for the coupling constant of the carbon atom adjacent to sulphur in the methane- and benzene-sulphonyl radicals has been found. From these values the sign of ε (the mechanistically significant parameter) for the various products can be obtained for the different compounds (**Vd**), (**VId**), and (**VIIc**) produced by the thermolysis of *O*-sulphinylated compound (**IVd**) (Scheme 2).

In the case of compound (**VId**) analysis of the enhanced absorption due to C-1 of the benzenesulphonyl group leads to a positive value for ε as appropriate for the recombination of F-pairs. This can then be used in sign equation (1) to analyse the polarisations of the *N*-methyl and carbonyl carbon atoms to give the sign of the hyperfine splitting constants shown for the acylnitroxyl radical (**X**). Strong polarisations were also observed in the *N*-methyl group of (**Vd**), (**VId**), and (**VIIc**). Analysis of the polarization gave the signs in Scheme 2.

Similar polarisations are found for the products formed from the decomposition of (**IVa** and **b**) (Table 3).

These results show that the sulphonamides (**V**) are formed by in-cage recombination of a geminate radical pair, whereas the amides (**VII**) are formed by hydrogen abstraction by the escaped amidyl radicals. The extensive polarisations in the *O*-sulphonylhydroxamic acids (**VI**) and the positive value of ε derived from the observed polarisation in the carbon adjacent to sulphur in the sulphonyl moiety indicate an in-cage recombination of the two persistent radicals (F-pairs) according to the mechanism shown in Scheme 3. This is the first example of the simultaneous low-temperature homolysis of two bonds in a given molecule, with subsequent combination of the escaped radicals (F-pairs).



Scheme 3.

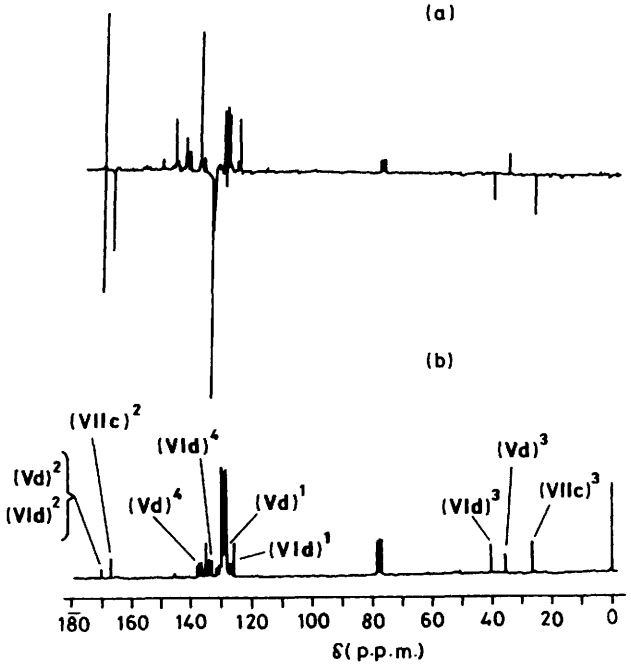


Figure 2. (a) ^{13}C N.m.r. spectrum of the thermolysis of *N*-methyl-*O*-phenylsulphinyl-4-chlorobenzohydroxamic acid (**IVd**) (10% w/v in $CDCl_3$) at 60 °C after 10 s. (b) ^{13}C N.m.r. spectrum of the above reaction after 5 min at 60 °C. The spectrum is assigned with reference to Table 3

Table 2. Composition (g) of the reaction mixture produced by the thermolysis of *N*-methyl-*O*-sulphinylated hydroxamic acids (**IVa—d**)

	(IV)	(V)	(VI)	(VII)	(VIII)	Yield (%)*	In-cage (%)
a	1.40	0.60	0.30	0.30		97.0	50.0
b	2.30	0.39	0.57	0.70	0.45	97.5	23.5
c	1.50	0.60	0.25	0.41		97.0	47.6
d	3.00	0.60	1.01	0.76	0.46	100.0	25.3

Eluant was cyclohexane–diethyl ether (9:1); flow rate 10 ml min^{-1}.
* Calculated for the amide group in the products (**V**)—(**VII**).

Table 3. CIDNP effects in the ^1H and ^{13}C spectra of *N*-acyl-*N*-methylsulphonamides (**V**), *N*-methyl-*O*-sulphonylhydroxamic acids (**VI**), and *N*-methylbenzamides (**VII**) from the thermolysis of *N*-methyl-*O*-sulphinylhydroxamic acids (**IV**) in $CDCl_3$ at 60 °C

Compound	Ar(C-1)	C=O	NCH_3	NCH_3	SO_2Ph(C-1)	SO_2CH_3
(**Va**)	E(+)*	A(+)	A(+)	E(+)		A(+)
(**Vb**)	E(+)	A(+)	A(+)	E(+)	A(+)	
(**Vd**)	E(+)[1]	A(+)[2]	A(+)[3]	E(+)	A(+)[4]†	
(**VIa**)	A(+)	E(+)	E(+)	A(+)		E(+)
(**VIb**)	A(+)	E(+)	E(+)	A(+)	E(+)	
(**VId**)	A(+)[1]	E(+)[2]	E(+)[3]	A(+)	E(+)[4]	
(**VIIIa**)	n.o.‡	E(−)	E(−)	A(−)		
(**VIIc**)	n.o.	E(−)[2]	E(−)[3]	A(−)		

* The values of ε are given in parentheses. † Superscript numbers for (**Vd**), (**VId**), and (**VIId**) refer to the assignment of peaks in Figure 2(b). ‡ No polarisation observed.

Experimental

Preparation of Starting Materials.—Benzene- and methanesulphinyl chlorides were prepared by the method of Douglass and Norton[10] with modifications suggested in our previous paper.[11] *N*-Methyl-4-toluohydroxamic acid[12] and *N*-methyl-4-chlorobenzohydroxamic acids[13] were prepared by published methods which involved the action of the appropriate acid chloride on *N*-methylhydroxylamine hydrochloride (Aldrich), in the presence of 2 equiv. of anhydrous sodium carbonate.

Preparation of N-*Methyl*-O-*phenylsulphinyl*-4-*toluohydroxamic Acid* (**IVb**).—This procedure is typical. A stirred equimolar solution of *N*-methyl-4-toluohydroxamic acid (1.06 g) and anhydrous triethylamine (0.61 g) in anhydrous dichloromethane (20 ml), cooled to −70 °C, was treated with a dichloromethane solution (5 ml) of benzenesulphinyl chloride (0.97 g). The mixture was stirred for 10 min, the temperature was allowed to rise to −10 °C, cyclohexane (25 ml) was added, and the mixture was filtered into a precooled flask (−70 °C). The solvent was removed by low-temperature (0 °C) evaporation under high vacuum and *N*-methyl-*O*-phenylsulphinyl-4-toluohydroxamic acid (**IVb**) was obtained as a crystalline solid (2.5 g, 96%), $\delta_H(CDCl_3)$ 2.36 (s, 3 H, $CH_3C_6H_4$), 3.59 (s, 3 H, NCH_3), and 7.00—7.80 (br, 9 H, ArH); $\delta_C(CDCl_3)$ 21.59 ($CH_3C_6H_4$), 41.59 (NCH_3), 129.37 (C-1, $CH_3C_6H_4$), 133.32 (C-1, SOC_6H_5), 141.78 (C-4, $CH_3C_6H_4$), and 171.87 p.p.m. (C=O).

Table 1 gives ^1H and ^{13}C n.m.r. data for *O*-sulphinylated hydroxamic acids (**IV—d**), *N*-acyl-*N*-methylsulphonamides

Table 4. Analytical data for *N*-acyl-*N*-methylsulphonamides (**V**), *N*-methyl-*O*-sulphonylhydroxamic acids (**IV**), and benzamides (**VIII**)

	Found (%)					Required (%)					
Compound	C	H	N	S	Formula	C	H	N	S	M.p. (°C)	Yield (%)
(Va)	53.0	5.8	6.4	14.0	$C_{10}H_{13}NO_3S$	52.9	5.8	6.2	14.1	112—113	71
(Vb)	62.3	5.1	4.8	11.6	$C_{15}H_{15}NO_3S$	62.2	5.2	4.8	11.1	99—100	77
(Vc)	43.7	4.3	5.9	12.6	$C_9H_{10}ClNO_3S$	43.6	4.1	5.7	12.9	152	85
(Vd)	54.2	3.8	4.7	10.2	$C_{14}H_{12}ClNO_3S$	54.3	3.9	4.5	10.4	98—99	81
(VIa)	49.0	5.4	5.6	13.8	$C_{10}H_{13}NO_4S$	49.4	5.4	5.8	13.2	93—94	80
(VIb)	58.6	4.9	4.5	10.7	$C_{15}H_{15}NO_4S$	59.0	5.0	4.6	10.5	98—99	77
(VIc)	40.8	3.6	5.2	12.0	$C_9H_{10}ClNO_4S$	41.0	3.8	5.3	12.2	143—144	79
(VId)	51.2	3.7	4.2	10.2	$C_{14}H_{12}ClNO_4S$	51.6	3.7	4.3	9.8	113—114	91
(VIIa)										143—144[a]	95
(VIIc)										160—161[b]	92

[a] Ref. 15. [b] Ref. 16.

(**Va—d**), *N*-methyl-*O*-sulphonylhydroxamic acids (**VIa—d**), and amides (**VIIIa** and **c**).

Unambiguous Synthesis of N-*Methyl*-N-(4-*toluoyl*)*benzenesulphonamide* (**Vb**).—*N*-Methylbenzenesulphonamide was prepared as follows. Benzenesulphonyl chloride (5.2 g) was treated dropwise with a 33% aqueous solution of methylamine (10 ml). The reaction mixture was stirred on a steam-bath for 15 min, cooled, and extracted with dichloromethane (×4). The dichloromethane fractions were combined, washed with water (×2), dried ($MgSO_4$), and evaporated to yield the product (4.66 g, 93%) as an oil, b.p. 220 °C at 0.25 mmHg;[14] $\delta_H(CDCl_3)$ 2.65 (s, 3 H, NCH_3), 5.32 (br, 1 H, NH), and 7.40—8.00 (br, 5 H, ArH); $\delta_C(CDCl_3)$ 29.23 (NCH_3), 127.20 (C-2, $SO_2C_6H_5$), 129.15 (C-3, $SO_2C_6H_5$), 132.71 (C-4, $SO_2C_6H_5$), and 138.82 p.p.m. (C-1, $SO_2C_6H_5$).

N-Methylmethanesulphonamide was prepared in a similar manner but the aqueous wash was left out of the isolation procedure.

The sulphonamide (1.0 g) and 4-toluoyl chloride (0.90 g) were heated together at 160 °C for 2 h. The mixture was cooled, diluted with ethyl acetate, washed with water (×2), dried ($MgSO_4$), treated with charcoal, and evaporated to yield an oil (1.5 g) which was crystallised from cyclohexane to yield a crystalline solid (**Vb**) (1.3 g, 77%), m.p. 99—100 °C (Found: C, 61.8; H, 5.1; N, 4.8; S, 11.6. $C_{15}H_{15}NO_3S$ requires C, 62.2; H, 5.2; N, 4.8; S, 11.1%); $\delta_H(CDCl_3)$ 2.36 (s, 3 H, $CH_3C_6H_4$), 3.32 (s, 3 H, NCH_3), and 7.30—7.90 (br, 9 H, ArH); $\delta_C(CDCl_3)$ 21.57 ($CH_3C_6H_4$), 35.75 (NCH_3), 131.51 (C-1, $CH_3C_6H_4$), 138.19 (C-1, $SO_2C_6H_5$), 142.86 (C-4, $CH_3C_6H_4$), and 171.61 p.p.m. (C=O); $\nu_{max.}$ (KBr disc) 1 690 (C=O), 1 352, and 1 160 cm^{-1} (SO_2); *m/z* 289 (M^+).

This method was used to prepare N-*methyl*-N-(4-*toluoyl*)-*methanesulphonamide* (**Va**), N-*methyl*-N-(4-*chlorobenzoyl*)-*methanesulphonamide* (**Vc**), and N-*methyl*-N-(4-*chlorobenzoyl*)-*benzenesulphonamide* (**Vd**). Table 1 shows relevant n.m.r., i.r., and mass spectrum data and Table 4 shows analysis data.

Unambiguous Synthesis of N-*Methyl*-O-*phenylsulphonyl*-4-*chlorobenzohydroxamic Acid* (**VId**).—To a stirred solution of *N*-methyl-4-chlorobenzohydroxamic acid (1.0 g) and anhydrous triethylamine (0.54 g) in anhydrous dichloromethane (10 ml), benzenesulphonyl chloride (0.95 g) was added dropwise. The mixture was left for 15 min, cyclohexane (10 ml) was added, the precipitated triethylamine hydrochloride was filtered off, and the solution was evaporated to yield the product as a crystalline solid (1.7 g) which was recrystallised from cyclohexane (1.6 g, 91%), m.p. 113—114 °C (Found: C, 51.2; H, 3.7; N, 4.2; S, 10.2. $C_{14}H_{12}ClNO_4S$ requires C, 51.6; H, 3.7; N, 4.3; S, 9.8%); $\delta_C(CDCl_3)$ 3.58 (s, 3 H, NCH_3) and 7.2—7.80 (br, 9 H, ArH); $\delta_C(CDCl_3)$ 40.06 (NCH_3), 133.64 (C-1, ClC_6H_4), 134.88 (C-1, $SO_2C_6H_5$), 137.62 (C-4, ClC_6H_4), and 170.11 p.p.m. (C=O); $\nu_{max.}$ (KBr disc) 1 690 (C=O), 1 380, and 1 195 cm^{-1} (S=O).

This method was used to prepare N-*methyl*-O-*methylsulphonyl*-4-*toluohydroxamic acid* (**VIa**), N-*methyl*-O-*phenylsulphonyl*-4-*toluohydroxamic acid* (**VIb**), and N-*methyl*-O-*methylsulphonyl*-4-*chlorobenzohydroxamic acid* (**VIc**).

Unambiguous Synthesis of 4-*Chloro*-N-*methylbenzamide* (**VIIc**).—A 33% aqueous solution of methylamine (20 ml) and 2 mol dm^{-3} sodium hydroxide (30 ml) were stirred together and cooled in an ice-bath. 4-Chlorobenzoyl chloride (5.0 g) was added dropwise over 15 min and the mixture was stirred for a further 15 min. The precipitate was filtered off and washed with ice-cold water. The product (5.1 g) was sucked dry and recrystallised from ethanol to yield needles (4.5 g, 92%), m.p. 160—161 °C (lit.,[16] 161°); $\delta_H(CDCl_3)$ 3.04 (d, 3 H, NCH_3), 6.70 (br, 1 H, NH), and 7.30—7.85 (br, 4 H, ArH); $\delta_C(CDCl_3)$ 26.94 (NCH_3), 132.95 (C-1, ClC_6H_4), 137.59 (C-4, ClC_6H_4), and 167.40 p.p.m. (C=O). This method was used to prepare *N*-methyl-4-toluamide (**IVa**).

Product Analysis of Thermal Rearrangement of N-*Methyl*-O-*phenylsulphinyl*-4-*toluohydroxamic Acid* (**IVb**).—*N*-Methyl-*O*-phenylsulphinyl-4-toluohydroxamic acid (**11b**) (2.3 g) was dissolved in anhydrous dichloromethane (15 ml) and stirred overnight at room temperature. The mixture was evaporated *in vacuo* and a sample was taken for ^1H n.m.r. analysis. The ^1H n.m.r. spectrum showed $\delta(CDCl_3)$ 2.36 (s), 2.37 (s), 2.94 (s), 3.32 (s), 3.52 (s), 7.04—8.04 (br, ArH). This spectrum would be consistent for a mixture containing principally *N*-methyl-*N*-(4-toluoyl)benzenesulphonamide (**Vb**), *N*-methyl-*O*-phenylsulphonyl-4-toluohydroxamic acid (**VIb**), and *N*-methyl-4-toluamide (**VIIa**) in the proportions of 13:19:24 respectively (based on N-CH_3 integral). The mixture was separated using flash chromotography.[17] The product (2.3 g) was taken up in dichloromethane (40 ml), silica (4.0 g; Merck; 230—400 mesh) was added, and the solvent removed *in vacuo* to leave a lump-free mobile powder. The powder was packed into a short medium-pressure liquid chromotography (m.p.l.c.) column (1.5 cm × 20 cm) on top of some pre-packed silica (*ca.* 10 g; Fisons; 60—120 mesh). The short m.p.l.c. column was eluted with light petroleum (b.p. 60—80 °C) until free of air. The main m.p.l.c. column (1.5 m × 1 000 cm) had been pretreated with cyclohexane–diethyl ether (9:1) and the sample was passed down it at a flow rate of 10 ml min^{-1}. Four major products were obtained. The first (0.45 g) was identified by comparison of its i.r. spectrum with that of authentic phenyl benzenethiosulphonate (**VIII**) prepared by the method of Barnard.[18] The second product was shown to be *N*-methyl-*N*-(4-toluoyl)benzene-

sulphonamide (**Vb**) (0.39 g) by comparison with a sample prepared by an unambiguous synthesis. The following data were found for the second product: $\delta_H(CDCl_3)$ 2.36 (s, 3 H), 3.32 (s, 3 H), and 7.20—8.00 (br, 9 H); $\delta_C(CDCl_3)$ 21.57, 35.60, 128.42, 128.90, 129.00, 129.25, 130.28, 131.84, 133.64, 138.65, 142.86, and 171.61 p.p.m.; $\nu_{max.}$ (KBr disc) 1 690, 1 352, and 1 160 cm^{-1}. Recrystallisation from cyclohexane gave needles, m.p. 99—100 °C [Found: C, 62.2; H, 5.2; N, 4.6; S, 11.3. $C_{15}H_{15}NO_3S$ (**Vb**) requires C, 62.2; H, 5.2; N, 4.8; S, 11.1%]. The m.p. was unaffected by mixing with an authentic sample.

The third product (0.7 g) yielded the following data: $\delta_H(CDCl_3)$ 2.40 (s, 3 H), 3.52 (s, 3 H), and 7.04—7.86 (br, 9 H); $\delta_C(CDCl_3)$ 21.47, 35.06, 40.89, 128.62, 128.90, 128.98, 129.26, 129.59, 133.69, 134.62, 142.03, and 171.40 p.p.m.; $\nu_{max.}$ (KBr disc) 1 690, 1 381, and 1 195 cm^{-1}. The product was recrystallised from cyclohexane to yield a crystalline product, m.p. 97—99 °C [Found: C, 59.1; H, 5.1; N, 4.6; S, 10.9. $C_{15}H_{15}NO_4S$ (**VIb**) requires C, 59.0; H, 5.0; N, 4.6; S, 10.5%], a mixed m.p. 98—99 °C.

The fourth product was identified as *N*-methyl-4-toluamide (**VIIa**) (0.70 g). The product was recrystallised from benzene–light petroleum (b.p. 40—60 °C) to yield needles, m.p. 143—144 °C (lit.,[15] 145 °C).

N-*Methyl*-O-*methylsulphinyl*-4-*toluohydroxamic acid* (**IVa**), N-*methyl*-O-*methylsulphinyl*-4-*chlorobenzohydroxamic acid* (**IVc**), and N-*methyl*-O-*phenylsulphinyl*-4-*chlorobenzohydroxamic acid* (**IVd**) were treated similarly (see Table 2 for a summary of the composition of reaction mixtures obtained.

Reaction between Methanesulphinyl Chloride and N-*Methyl*-4-*toluohydroxamic Acid.*—*N*-Methyl-4-toluohydroxamic acid (1 g) and anhydrous triethylamine (0.61 g) in anhydrous dichloromethane (10 ml) were cooled to −70 °C. To the stirred solution methanesulphinyl chloride (0.59 g) in dichloromethane (2 ml) was added dropwise. The reaction mixture was filtered after 10 min and stirred overnight at room temperature. The solvent was removed *in vacuo* and the product (1.40 g) was submitted for ^1H n.m.r. analysis. The ^1H n.m.r. spectrum showed that the mixture was the same as that obtained when the intermediate was isolated and then allowed to rearrange; this was found to be general for all the rearrangements.

E.s.r. Experiment.—A JEOL PE IX e.s.r. spectrometer was employed. A 10% w/v solution of (**IVa**) in $CHCl_3$ was placed in a precooled e.s.r. tube (0 °C) and placed in the cavity of the spectrometer at *ca.* 25 °C. A strong signal due to the acylnitroxyl radical (**X**) was observed within 30 s. This radical persisted for *ca.* 20 min. The *g* value was measured using diphenylpicrylhydrazyl as reference (*g* 2.0036).

CIDNP Experiments.—Solutions of (**IVa, b, d**) (10 w/v in $CDCl_3$) were prepared at −70 °C and filtered into a precooled 10 mm n.m.r. tube. The tube was placed immediately into the probe (at 60 °C) of a Brucker WM 200 SWB n.m.r. spectrometer operating at 50.3 MHz. The ^{13}C n.m.r. spectra were recorded using the pulsed Fourier transform mode. About 15 s elapsed when 75 transients were accumulated (*ca.* 5 μs pulse, 22.5° flip angle, 0.7 s repetition rate, 12.5 kHz spectral width, 16 K data points). The accumulated f.i.d. was stored and the experiment was repeated. The analogous unpolarised spectrum was obtained after 5 min.

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