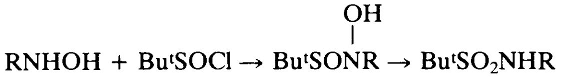
The Reaction between *N,N*-Dialkylhydroxylamines and Sulphinyl Chlorides

Malcolm R. Banks and Robert F. Hudson

Chemical Laboratory, University of Kent at Canterbury, Canterbury, Kent CT2 7NH, U.K.

The reaction of *N,N*-dialkylhydroxylamines with sulphinyl chlorides proceeds *via* an *O*-sulphinylated hydroxylamine intermediate, which has been isolated and characterised by n.m.r. spectroscopy; rearrangement of this intermediate to the sulphonamide has been shown to involve an aminyl radical.

It has been known for some time that hydroxylamine and *N*-substituted hydroxylamines react with sulphinyl chlorides under mild conditions to give sulphonamides.[1] The mechanism of this reaction is not established, but in view of the rapid reaction of *O*-methyl-*N*-alkylhydroxylamines to give the corresponding *N*-methoxysulphinamide[2] a heterolytic mechanism involving nucleophilic nitrogen has been assumed. The absence of polarised ^{1}H n.m.r. spectra during the reaction of t-butylsulphinyl chloride with *N*-substituted hydroxylamines [see equation (1)] was noted.[3]



$$\mathrm{RNHOH + Bu^tSOCl \rightarrow Bu^t\overset{OH}{\overset{|}{S}}ONR \rightarrow Bu^tSO_2NHR} \quad (1)$$

In view of the possibility of a radical mechanism following recent observations on the reactions of sulphinyl chlorides with oximes,[4] *N*-hydroxycarbamates,[5] and *N*-phenylbenzhydroxamic acid,[6] we have investigated the reaction of *N,N*-dialkylhydroxylamines with methyl- and phenylsulphinyl chloride (see Scheme 1). At −70 °C in CH_2Cl_2 in the presence of triethylamine, an intermediate was isolated and characterised by ^{1}H and ^{13}C n.m.r. spectra as the *O*-sulphinylated hydroxylamine (I).

Thus the ^{13}C spectra showed absorption at $\delta \sim 50$ for the α-carbon of the dialkylamino group, which is close to the value for the corresponding hydroxylamine, *e.g.* δ 53.9 for *N,N*-diethylhydroxylamine. Electron attracting substituents produce large upfield shifts *e.g.* δ 37.6 for *N,N*-dimethylmethanesulphonamide. On this and similar evidence[7] the alternative structure for the intermediate, $R_2N^+(O)SOR$ is ruled out.

The intermediate (I) rearranges above 0 °C to give a mixture of products including sulphonamide and imine. For example phenylsulphinyl chloride and *N,N*-dibenzylhydroxylamine give the following isolated products: $(PhCH_2)_2NSO_2Ph$ (21% yield); $PhCH_2N{=}CHPh$ (27%); PhCHO (6%); $PhSO_3H$ (9%); and $PhSO_2SPh$ (15%). The yield of sulphonamide is dependent on the substituent as shown in Table 1.

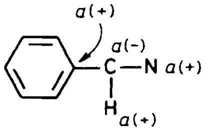
$$\mathrm{R_2NOH + R'SOCl \xrightarrow{i} \underset{(I)}{R_2N\text{–}O\text{–}S(:O)\text{–}R'} \xrightarrow{ii} R_2NSO_2R'}$$

R = Me, Et, or $PhCH_2$
R′ = Me or Ph

Scheme 1. i, CH_2Cl_2, Et_3N, −70 °C; ii, CH_2Cl_2, 25 °C.

These results show that the formation of sulphonamide is accompanied by varying yields of imine and sulphinic acid produced in an elimination. Sulphinic acids are known to decompose spontaneously[8] with the formation of sulphonic acid, thiosulphonate, and water. Water produced in this reaction decomposes part of the imine to give benzaldehyde.

Evidence for free-radical intermediates was found by the decolourisation of diphenylpicrylhydrazyl (DPPH) in the course of the reaction, and by enhanced polarisation of the methylene protons and of carbon nuclei in the amino and sulphonyl groups of the sulphonamide, summarised in Table 2.



(1)

From the *g*-values of the sulphonyls[4] and aminyls,[9] and the assumed signs of the hyperfine coupling constants, *a*, in the aminyl radical (**1**), the enhanced absorptions for methylene protons and the C-1 carbon atom of the phenyl ring show[10] that the sulphonamide is formed, at least in part, by in-cage recombination. This is the first example of a homolytic rearrangement involving an aminyl radical.

No polarisations were detected in the ^{1}H and ^{13}C nuclei of the imine. This indicates that the elimination proceeds by a symmetry-allowed (6e) cyclic mechanism, although a radical-cage process cannot be completely ruled out.

As a result of this work we come to the following general conclusions. *N,N*-Disubstituted hydroxylamines react through their nucleophilic oxygen to give *O*-sulphinylated hydroxylamines which rearrange to the sulphonamide at least

Table 1. Yields of sulphonamide, R_2NSO_2R', in the reaction of sulphinyl chlorides with *N,N*-disubstituted hydroxylamines.

R	R′	Isolated yield/%
Me	Me	70
Me	Ph	63
Et	Me	62
Et	Ph	38
$PhCH_2$	Me	45
$PhCH_2$	Ph	21

Table 2. CIDNP effects in the reaction of *N,N*-dibenzylhydroxylamine and sulphinyl chloride in $CDCl_3$ at 60 °C.[a]

	Ph(C-1)	CH_2(H)	SO_2Me(C)	SO_2Ph(C-1)
$(PhCH_2)_2NSO_2Me$	A	A	E	—
$(PhCH_2)_2NSO_2Ph$	A	A	—	E

[a] A = Enhanced absorption; E = enhanced emission.

in part by a radical-cage mechanism. Monosubstituted hydroxylamines (and hydroxylamine) also react with sulphinyl chloride to give a hydroxysulphinamide but the mechanism of the rearrangement assumed to be involved remains obscure.

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