4-Nitrosopyridine 1-Oxide and its Derivatives: A New Range of Spin-traps

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4-Nitrosopyridine 1-oxide and its derivatives have been shown to be highly efficient water-soluble spin-traps for *C*- and *O*-centred radicals giving rise to persistent nitroxides.

Although some substituted aromatic nitroso-compounds *e.g.* nitrosodurene give rise to fairly stable nitroxides when used as spin-traps,[1] they suffer from the disadvantage of low solubility in alcohols (zero in water) thus requiring a co-solvent when

Table 1. Spin-adducts of 4-nitrosopyridine 1-oxide,[a] $ONC_5H_4\overset{\cdot}{N}OR$.

R	a_N	a_N^{ring}	a_H^β	$a_H^{2,6}$	$a_H^{3,5}$	a_N^b	a_N^c
$Me_3\overset{\cdot}{C}$[d]	9.73	2.46	—	1.23	2.46	10.5	13.1
$Me_2\overset{\cdot}{C}CN$[d]	9.6	2.28	—	1.38	2.76	10.1	12.8
$Ph_2\overset{\cdot}{C}H$[d]	8.9	2.7	4.8	1.35	2.7	9.35	12.7
$Bu^tO\cdot$[e]	11.4	2.9	—	1.54	3.2	11.9	17.0
$MeO\cdot$[f]	11.6	3.2	—	1.2	3.2	—	—
$EtO\cdot$[f]	11.63	3.2	—	1.5	3.2	—	—

[a] [Spin-trap] 0.05—0.10 M, [radical source] 0.01—0.10 M. [b,c] a_N values for 2,6-dimethyl- and 3,5-dimethyl-pyridine 1-oxide, respectively. Full hfs have been obtained from computer-simulated spectra. [d] Produced by thermolysis in benzene of Bu^tNO, $[Me_2C(CN)]N_2$ and $(Ph_2CH)_2N_2$, respectively. [e] In toluene. [f] In the corresponding alcohol.

used in polar media.[2] In connection with other work we required a nitroso spin-trap soluble in alcohols and in water which would give persistent nitroxides. 4-Nitrosopyridine 1-oxide and some of its derivatives fulfil these and other desirable properties admirably. We have analysed the e.s.r. spectra produced when these compounds react with a range of carbon- and oxygen-centred radicals.

4-Nitrosopyridine 1-oxide[3] and its 2,6-dideuterio, 2,6-dimethyl, and 3,5-dimethyl analogues[4,5] are green monomeric solids,† stable under nitrogen in laboratory fluorescent lighting for months. Their solutions in a range of solvents (including water) are also light-stable under nitrogen for several days, thus contrasting with the photo-instability of solutions of many aromatic nitroso-compounds.[6] One further advantage these compounds possess is that being monomeric solids they are also completely monomeric in solution.

When 4-nitrosopyridine 1-oxide reacts in benzene with t-butyl, dimethylcyano, and diphenylmethyl radicals (generated thermally by standard methods) the nitroxides produced give rise to complex but well resolved e.s.r. spectra, whose intensity remains constant for several hours. The hyperfine splittings (hfs) shown in Table 1 were derived from computer-simulated spectra. The electronic influence of the 1-oxide function is clearly reflected in the low hyperfine splittings of the nitroxide nitrogens, that for the t-butyl adduct a_N 9.73 G comparing with a_N 13.3 G for the corresponding phenyl nitroxide.[7]

The e.s.r. spectra of the nitroxides obtained from $[2,6-^2H_2]$-4-nitrosopyridine 1-oxide have confirmed the analyses presented in Table 1 for the $^1H_2$ compounds, in particular the positions assigned to the ring proton splittings.

Although these compounds are efficient spin-traps for C-centred radicals it is as scavengers of O-centred radicals that their properties are most striking. When di-t-butyl peroxalate thermolyses in toluene at room temperature

nitrosodurene traps the benzyl radical. When 4-nitrosopyridine 1-oxide is used in place of nitrosodurene as the spin-trap it is the t-butoxyl radical which is trapped. No trace of a benzyl adduct can be detected in the e.s.r. spectrum. 4-Nitroso-3,5-dimethylpyridine 1-oxide behaves similarly and the hfs of the nitrogen of the nitroxyl produced (17.0 G as against 11.3 G for the parent compound) clearly shows the deconjugating effect of the ring methyl groups.

The efficiency of 4-nitrosopyridine 1-oxide as a spin-trap for O-centred radicals is further demonstrated when lead tetra-acetate reacts with methanol or ethanol in its presence. The e.s.r. spectra of the nitroxyls produced thereby are those expected for the alkoxyl adducts (see Table 1). No trace of the hydroxyalkyl adducts could be detected from the spectra. In contrast, when 2-methyl-2-nitrosopropane is used as a spin-trap in liquid alcohols the hydroxyalkyl adduct is obtained either alone[8] or in addition to that of the alkoxyl radical.[9]

The ability of these compounds to scavenge O-centred radicals before they can abstract a hydrogen atom from two quite different types of solvent *and* yield nitroxides that persist for several hours should make them a useful addition to the range of spin-traps.

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† Preparations were by standard methods although not those described in the literature.[4,5] All compounds gave correct elemental analysis (C, H, and N) and ^1H n.m.r. spectra consistent with their structure. Our m.p. values for the 2,6- and 3,5-dimethyl derivatives are 108—109 °C and 110 °C (decomp.), respectively and compare with 142—143 °C (only N analysis)[4] and 203 °C (no analysis).[5]