Poly(ß-phosphorylated nitrones): preparation and characterisation of new class of spin trap

Robert P. Lauricella, Béatrice N. Tuccio, Valérie M. Roubaud, and Jean-Claude H. Bouteiller

UMR-CNRS 6517, Universités d'Aix Marseille 1 et 3, case 541, Faculté de St. Jérôme, 13397 Marseille cedex 20, France. robert@SREPIR1.univ-mrs.fr

Four new poly-(β -phosphorylated nitrones), the 1, 3, 5- tri [(N-(1-diethylphosphono)- 1-methylethyl) N-oxy-aldimine] benzene (TN) 1, the 1,3-di [(N-(1-diethylphosphono)-1-methylethyl) N-oxy aldimine] benzene (MDN) 2, the 1, 4 di [(N- (1-diethylphosphono)- 1-methylethyl) N-oxy aldimine] benzene (PDN) 3, and the 1, 2- di [(N-(1-diethylphosphono)-1-methylethyl) N-oxy aldimine] benzene (ODN) 4, derived from the mono-nitrone N-benzylidene-1-diethoxyphosphoryl-1-methylethylamine N-oxide (PPN) 5, were synthesised.

$$(EtO)_{2}(O)P \longrightarrow HC \longrightarrow P(O)(OEt)_{2}$$

$$(EtO)_{2}(O)P \longrightarrow HC \longrightarrow P(O)(OEt)_{2}$$

$$(EtO)_{2}(O)P \longrightarrow P(O)(OEt)_{2}$$

$$(EtO)_{2}(O)P \longrightarrow P(O)(OEt)_{2}$$

$$ODN 4$$

The capacity of 1-4 to act as spin trapping agents was investigated in phosphate buffers at pH 5.8 and 7.2. Complex EPR spectra of spin adducts have always been obtained with the ortho-dinitrone 4. The three other compounds trapped efficiently superoxide and several carbon-centred radicals, giving mono-spin adducts, although only weak signals were obtained with the hydroxyl radical. When the spin trap concentration was kept below 1 mmol.dm-3, the formation of di-radicals also occurred. The half-lives of the superoxide spin adducts of 1-3 were in the range 5 - 12 min. and did not significantly change between pH 5.8 and 7.2. A competitive kinetic study showed that the tri-nitrone 1 trapped the methyl radical 1.9 time more rapidly than both a-(4-pyridyl-1-oxide)-N-terbutylnitrone (POBN) and 5-diethoxyphosphory-5-methyl-4,5-dihydro-3H-pyrrole N-oxide (DEPMPO) at pH 7.2.

V. Roubaud, H. Dozol, C. Rizzi, R. Lauricella, J.C. Bouteiller, B. Tuccio, *J.Chem.Soc.Perkin Trans.*2, 2002, 958-964.