

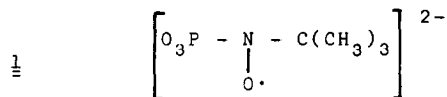
CHARACTERISATION OF A CONTAINING PHOSPHORUS NITROXIDE FREE RADICAL

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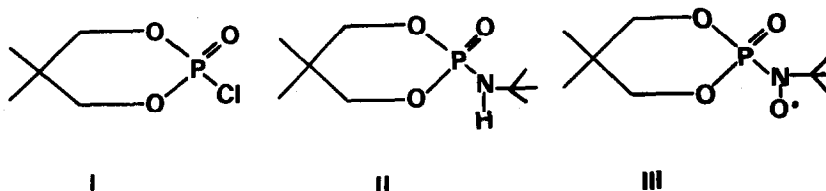
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Recently, G. ADEVIK and C. LAGERCRANTZ (1) have reported the spin trapping by nitroso scavengers of the radical ion $\cdot\text{PO}_3^{2-}$ formed by γ -irradiation of sodium phosphite. This reaction leads to nitroxide radicals stable enough to be detected by ESR spectroscopy. The structure (1) was assigned to the observed ra-



dical. In order to confirm the structure, and in view of recent interest in spin labelled phosphates (2) (3), we tried to prepare by chemical synthesis nitroxide radicals in which the nitrogen atom is directly bonded to a phosphorus atom.

According to the general procedure given by R.S. EDMUNDSON and coworkers (4), 2 t-butylamino-5,5 dimethyl-2-oxo-1,3,2 dioxaphosphorinane (II) is obtained by reaction of t-butylamine and 2-chloro-5,5 dimethyl-2-oxo-1,3,2 dioxaphosphorinane (I)*.



Some of the possible ways of preparing nitroxide free radical from the corresponding amine have been tried. When either H_2O_2 with and without phosphotungstic acid or PbO_2 (5) is reacted with amine (II), no radical is

* Compound II gives a satisfactory microanalysis, the nmr spectrum is in agreement with the formula, and the mass spectrum exhibits a peak at the molecular weight.

observed, but the reaction of (II) with p-nitrobenzoic acid (6) leads to the formation of a nitroxide free radical.

At room temperature, in an esr tube a mixture of 51 mg of (II) and of 27 mg of p-nitrobenzoic acid in 200 μ l of methylenechloride shows a six-line free radical esr spectrum (fig. 1). The intensity of the signal increases for a five hours period, then decreases with no change in the structure, nor appea-

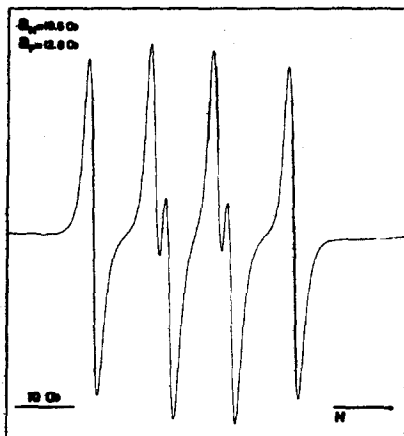


Fig. 1 : esr spectrum of the nitroxide free radical (III).

rance of any other signal. The maximum concentration observed for the radical is approximately $M/500$.

The g value (2.0066 in methylene chloride) clearly indicates that the free radical obtained is a nitroxide free radical (7). The six-line signal is interpreted as being due to the coupling of the unpaired electron with a nitrogen atom ($S = 1$, $a_N = 10.5$ Oe) and with a phosphorus atom ($S = 1/2$, $a_P = 12.8$ Oe). Such a spectrum is in agreement with the formula (III)*. The concentration obtained in this preparation does not allow the isolation of the free radical (III).

It must be pointed out that the hyperfine coupling constants reported in (1) show a_N (13.4 Oe) greater than a_P (12.0 Oe), which is opposite to the order reported for the radical (III) ($a_N = 10.5$ Oe, $a_P = 12.8$ Oe).

* However an open chain structure cannot be ruled out.

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