



0.5 hour, followed by a solution of ethyleneimine (1.72 g, 0.04 mole) in dry benzene (40 ml) which was added during 0.8 hour at 6–8 °C. After stirring at 10 °C for 1 hour, the mixture was stirred at room temperature for 7 days. The suspension was then filtered to remove the triethylamine hydrochloride (5.23 g, 95% of theory), and the filtrate was concentrated on a rotating evaporator at 40 °C (25 mm Hg). The remaining red oil was dissolved in benzene, and the solution chromatographed on an alumina column (1 g oil/10 g Al<sub>2</sub>O<sub>3</sub>) using a 4:1 (v/v) solution of benzene and ethyl acetate as eluent. Concentration of the eluted solution gave a red oil which solidified on storage in a refrigerator overnight to a red solid, 3.7 g (61%); m.p. 56–60 °C (dec.). EPR: 3 equidistant lines of equal intensity,  $a_N = 15$  G.

#### Analysis

C<sub>13</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>P:

Calcd: C 51.64 H 8.33 N 13.90 Mol. wt. 302.32,

Found: C 51.43 H 8.01 N 13.60 Mol. wt. 309.

*O*-(1-Oxyl-2,2,6,6-tetramethyl-4-piperidyl)-*N,N'*;  
*N',N'*-bis(ethylene)-phosphorodiamidothioate  
(5, X = S)

A solution of phosphorus thiochloride (3.39 g, 0.02 mole) in dry benzene (100 ml) was cooled to 6–8 °C, and vigorously stirred under anhydrous conditions. A solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl<sup>6</sup> (1, 3.44 g, 0.02 mole) and

triethylamine (2.02 g, 0.02 mole) in dry benzene (100 ml) was then added during 1.0 hour. After stirring at 10 °C for 1.5 hour, the reaction mixture was allowed to warm up to room temperature, and the stirring continued for 24 days. The precipitated triethylamine hydrochloride was removed by filtration (2.75 g, 100% of theory). The filtrate containing *O*-(1-oxyl-2,2,6,6-tetramethyl-4-piperidyl) phosphorodichloridothioate (3, X = S, 0.02 mole) in dry benzene (200 ml) was cooled to 5–8 °C and vigorously stirred. A solution of ethyleneimine (1.72 g, 0.04 mole) and triethylamine (4.04 g, 0.04 mole) in dry benzene (70 ml) was added during 1.5 hours. After stirring for 2 hours at 10 °C, the reaction mixture was allowed to warm up to room temperature, and the stirring continued for 6 days. The reaction mixture was then filtered to remove the triethylamine hydrochloride (5.28 g, 96% of theory). After removal of the solvent on a rotating evaporator at 40 °C (25 mm Hg), the remaining red oil was dissolved in dry benzene, and the solution chromatographed on a alumina column (1.0 g oil/10 g Al<sub>2</sub>O<sub>3</sub>) using a 4:1 (v/v) solution of benzene and ethyl acetate as eluent. Concentration of the eluted solution gave a red solid, 3.0 g (50%); m.p. 91–93 °C (dec.). EPR: 3 equidistant lines of equal intensity,  $a_N = 15$  G.

#### Analysis.

C<sub>13</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>PS:

Calcd: C 49.06 H 7.86 N 13.20 Mol. wt. 318.38,

Found: C 49.07 H 7.76 N 13.02 Mol. wt. 315.

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<sup>2</sup> Mention of commercial or proprietary names in this paper does not constitute an endorsement or quality preference of these products over other commercial products of the same chemical composition by the authors, editors, or publishers.

<sup>3</sup> H. M. Swartz, *Advances Cancer Res.* **15**, 227 [1972], and references therein.

<sup>4</sup> C. G. Schmidt, *Krebsforschung und Krebsbekämpfung*, eds. H. E. Bock and U. Dold, vol. 6, p. 309, Urban & Schwarzenberg, München 1967, and references therein.

<sup>5</sup> The Merck Index, ed. P. G. Stecher, 8th edition, p. 1073, Merck & Co., Inc., Rahway, N.J., USA 1968.

<sup>6</sup> E. G. Rozantsev, *Free Nitroxyl Radicals*, pp. 185, 214, and references therein, Plenum Publ., New York 1970.

<sup>7</sup> A. B. Shapiro, A. A. Kropacheva, V. I. Suskina, B. V. Rozynov, and E. G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 864.