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**Carboxylation of the Nitroxide Radical of 2,2,6,6-Tetramethyl-4-piperidone-1-oxyl with Carbon Dioxide and Potassium Phenoxide, and the Physical Properties of the Products\***

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A stable nitroxide radical containing active methylenes, 2,2,6,6-tetramethyl-4-piperidone-1-oxyl (I), was found to be carboxylated by potassium phenoxide and carbon dioxide in an aprotic solvent (N,N-dimethylformamide), producing new nitroxide compounds. The mono- or dicarboxylate was formed selectively, depending on the molar ratio of the substrate to potassium phenoxide.

The ultraviolet and visible spectra of the monomethyl- (II) and dimethylester (III) of the carboxylates as well as those of I and 2,2,6,6-tetramethylpiperidine-1-oxyl (IV) were investigated in various solvents. The results indicated that II exists mainly as the keto form in a polar solvent, and as the enol form in a nonpolar solvent, while the enol form of III is predominant in all the solvents tested. The nitrogen hyperfine coupling constants,  $A_N$ , of I—IV in the electron spin resonance spectra were determined, and the results are discussed in terms of the keto-enol equilibrium.

Furthermore, the distribution coefficients of these nitroxide radicals between hexane and water were measured to assess the potential suitability of these newly formed nitroxide radicals for use as spin labels or probes.

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