ABSTRACT. 1-(4'-Pyridyl)-4-pyridone (1) was prepared from 4-pyridone and acetic anhydride by the method of Arn dt and Kalischek. When 1 is irradiated at 300 nm in deaerated solutions of 1° or 2° alcohols in the cavity of an ESR spectrometer, an intense blue radical forms immediately. Emission and quenching studies indicate that this radical forms through an $S(\pi,\pi^*)$ state of 1. Further studies revealed that the blue radical is identical with the alkylviologen cation radical. The presence of water in these reaction mixtures results in the formation of a dimer product determined to be a salt of 11,12-di(4-pyridyl)-11,12-diazatricyclo[5.3.1.1$^{2,6}$]dodecane-4,9-dione. Viologen forms by a very rapid 4,4' coupling–elimination reaction of the radical form of 1, while the dimer results from a head-to-tail dimerization of two molecules, very likely with an aziridine structure, solvated by water molecules. Cyclic voltammetry shows that 1 undergoes irreversible reduction at -1.2V and immediately converts to viologen after one cycle with the related reversible cyclic voltammogram. Irradiation of 1 with chloropyridine in 2-propanol yields a polypyridine that has different physical properties than the polypyridine obtained from the thermal polymerization of chloropyridine alone. A precipitate forms which was shown to be a radical which when dissolved in water undergoes a series of spontaneous color changes.

INTRODUCTION

As a part of a continuing study on the photoinitated radical forming reactions of six membered N-heterocycles, we prepared and studied 1-(4'-pyridyl)-4-pyridone (1) and its protio and N-methyl derivatives. When 1 is irradiated as the N-protio or N-methyl salt in deaerated solutions of 1° or 2° alcohols, an intense blue radical is obtained that has an ESR spectrum similar to that of methylviologen cation radical (2). We became interested in determining the structure of this blue radical with the hope that 1 might be a precursor to 2 in the photochemical reaction with alcohol

In the past, 4,4'-bipyridinium salts have been studied extensively, especially with regard to the ease with which they undergo one electron reduction. 1,1'-Dimethyl-4,4'-bipyridinium dichloride (methylviologen) is probably the most studied member of this family of compounds because of its widespread use as a herbicide, electron
transfer indicator, and electron carrier in solar energy conversion systems. We were also interested in other reactions of the radical of 1 both in relation to its dimerization and as an initiator of polymerization with chloropyridine.

\[
\text{O} \quad \text{N} \quad \text{A} \quad \text{N} \\
\text{CH}_3 \quad \text{N} \quad \cdot \quad + \quad \text{N} \quad \text{CH}_3
\]

\[
1 \\
2
\]

MATERIALS AND METHODS

All solvents used in this study were analytical grade. The 4-pyridone was technical grade (90%) obtained from the Aldrich Chemical Co. All ESR spectra were taken on either a Varian E104 or a Bruker ER 220D spectrometer. The radical of 1 was generated in situ by irradiation of solutions of the base in the cavity of an ESR spectrometer. ESR spectra were taken either with a flat, quartz flow-through cell using solutions that had been deaerated by nitrogen bubbling for a minimum of twenty minutes before irradiating or with pyrex tubes which were 5 inches long and 2 mm i.d. and subjected to three freeze-vacuum-thaw cycles before irradiating. Irradiations were carried out with a 1000-W high pressure mercury lamp which had the same orientation with respect to the sample for each run and focused on the sample.

RESULTS

When a deaerated alcoholic solution of 1 is irradiated at 300 nm, the solution turns dark blue immediately. When this irradiation is performed with the sample in the cavity of an ESR spectrometer, a complex spectrum is obtained which is very similar to that of methylviologen cation radical. Illumination studies indicate that radical formation occurs from an \(S(\pi, \pi)\) state of 1. The radical obtained showed strong absorption in the UV-visible spectrum at 385, 395, and 605 nm \((\varepsilon_m = 11,200, 4:1 2\text{-}\text{propanol/H}_2\text{O})\) and was similar to the spectrum of 2.

Final confirmation of the structure of this radical was obtained by an ENDOR study which showed that the hyperfine splitting constants of the radical obtained from 1 are the same as those of the ESR spectrum of 2.