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AN EFFICIENT PREPARATION OF 4,4'-DICARBOXY-2,2'-BIPYRIDINE

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Abstract
A convenient and high yield preparation of 4,4'-dicarboxy-2,2'-bipyridine from the oxidation 4,4'-dimethyl-2,2'-bipyridine with potassium dichromate in sulfuric acid is reported.

Introduction

Due to their participation as sensitizers in various photoredox schemes, tris- ruthenium(II) chelates of 2,2-bipyridine, and its derivatives, have abounded in the recent literature[1]. One of the more interesting complex ions of this type is the 4,4'-bis-(2,2'-bipyridine-*N,N'*)(4,4'-dicarboxy-2,2'-bipyridine-*N,N'*) ruthenium(II) cation, and its photophysical and photochemical properties have been the subject of several recent studies[2-6]. Early reports concerning the photophysical properties and the acidity constants of the ion, in both the ground and excited

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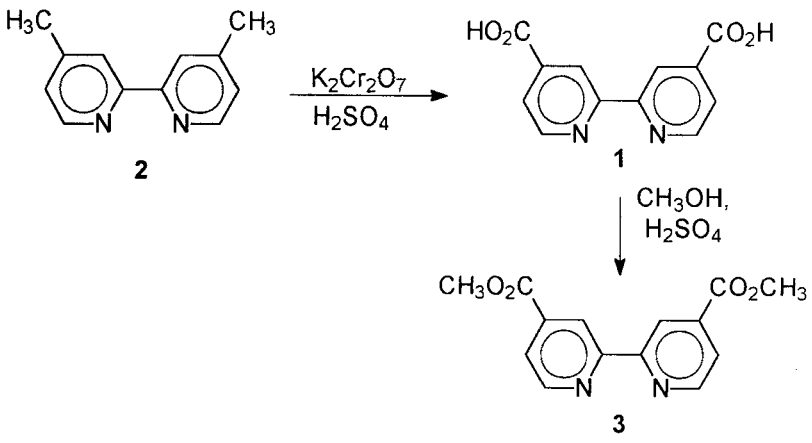
state, suggested the intriguing possibility of achieving proton transfer from the ion while in the excited state[2,3]. Some of these earlier results were questioned[4,5], and reproducibility problems were traced back to the preparation of the ligand **1** (4,4'-dicarboxy-2,2'-bipyridine **1**, Scheme 1). With these difficulties resolved[4], the complex ion was found to be an effective catalyst in the photoreduction of water[5].

In these earlier works, **1** was obtained from permanganate oxidation of 4,4'-dimethyl-2,2-bipyridine[3,7-9] **2**. The methodology was then modified and improved by Sasse and co-workers[4], who doubled the reported yield of the diacid **1** (from 26 to 52%) by performing the oxidation in aqueous acid. In addition they also developed an effective purification of **1**, and noted the formation of several impurities common to permanganate oxidations of **2**, most notably 4-methyl-4'-carboxy-2,2'-bipyridine[4].

We have recently embarked on a new project in which we require substantial quantities of 4,4'-dicarboxy-2,2'-bipyridine. The best available preparation of **1** was the procedure of Sasse[4], but we found that it was awkward to perform on a large scale. In addition, it also resulted in an incomplete oxidation, even after 12 hours at reflux, and gave only a moderate yield of **1**.

Quite by accident, we saw mention of a procedure in which 4,4'-dimethyl-2,2'-bipyridine was oxidized to **1** using chromium (VI) oxide in 90% yield[10], but no details were given except a reference to the oxidation of a substituted pyridine[11]. Thus we decided to explore chromium based oxidations of **2**, and on our first attempt, using the procedure described in the Experimental Section we obtained a yield of 90%.

The diacid **1**, is soluble in acid and base, and almost completely insoluble in organic solvents, alcohols and water. Because of this insolubility, we chose to evaluate samples of **1** by HRMS, and as its dimethyl ester derivative **3**. The ^{1}NMR spectrum, however, does agree with that previously reported[4], and shows only aromatic and carboxyl protons. This is significant because the major impurity in the permanganate based



Scheme 1

oxidations is 4-methyl-4'-carboxy-2,2'-bipyridine[4], which has a signal at δ 2.89, corresponding to the methyl protons. Apparently, the dichromate based procedure results in a more complete oxidation, than do those utilizing potassium permanganate. The mass spectrum of **1** shows the expected molecular ion at *m/z* 244, (70%), and the base peak results from loss of CO_2 (M^+ - 44, *m/z* 200, 100%). The dimethyl ester **3** can be prepared in 80% from samples of **1**, as obtained by the use of our procedure, and its properties agree with those previously reported[12].

Experimental

Samples of **2** were prepared from 4-picoline using a previously reported procedure[9], and always sublimed prior to use. All other reagents were used as received from chemical suppliers. NMR spectra were recorded on a Bruker AC 250, and mass spectra on a Kratos MS-50 triple analyzer.

Preparation of 4,4'-Dicarboxy-2,2'-Bipyridine (1)

To a stirring solution of sulfuric acid (98%, 125 mL), 5.0 g (20.5 mmoles) of 4,4'-dimethyl-2,2'-bipyridine was added. With efficient stirring, 24 g (81.5 mmoles) of potassium dichromate was then added in small portions, such that the temperature remained between 70 and 80 °C. Occasional cooling in a water bath was usually necessary during the addition of potassium dichromate. After all the dichromate was added, the reaction was stirred at room temperature until the temperature fell below 40 °C. The deep green reaction mixture was poured into 800 mL of ice water and filtered. The solid was washed with water until the filtrate was colorless and allowed to dry. The resulting light yellow solid was then further purified by refluxing it in 170 mL of 50% nitric acid for 4 hours[12]. This solution was poured over ice, diluted with 1 L of water and cooled to 5 °C. The precipitate was filtered, washed with water (5 X 50 mL), then acetone (2 X 20 mL) and allowed to dry giving 6.2 g (94 %) of **1** as a fine white solid.

mp. > 325°, HRMS, Calc. for $C_{12}H_8O_4N_2$ 244.048406. Found: 244.04810

m/z 244.04810 (M^+ 70.0%), 200.05870, (100.0%, M-CO_2, $C_{11}H_7O_2N_2$), 172.03989 (19.2%, $C_{10}H_6NO_2$), 155.06059 (16.7%, $C_{10}H_7N_2$), 51.02339 (24.4%, C_4H_3).

^{1}H NMR is in agreement with that reported previously[4].

Preparation of 4,4'-Bis-(Methoxycarbonyl)-2,2'-Bipyridine (3)

The dimethyl ester of **1** was prepared by an existing literature method and obtained as colorless crystals. mp. 207-209° in 80% yield (lit. 208-210°, 73%)[13]

^{1}H, ($CDCl_3$, 250 MHz) : δ 3.71 (s, 6 H, CO_2CH_3), δ 7.91 (dd, $J_{5,6}$ = 5.0, $J_{3,5}$ = 1.49 Hz, 2 H, H_5), δ 8.87 (d, $J_{5,6}$ = 5.0 Hz, 2 H, H_6), δ 8.97 (d, $J_{3,5}$ = 1.49 Hz, 2 H, H_3), ^{13}C($CDCl_3$), δ 53.73, 120.545, 123.21, 138.62, 150.12, 156.48, 165.07

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