

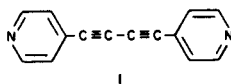
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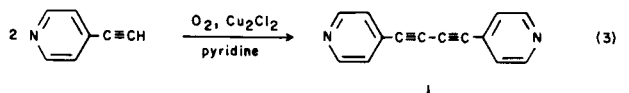
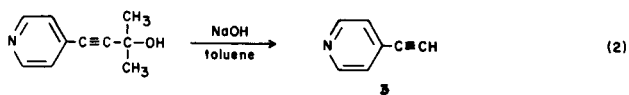
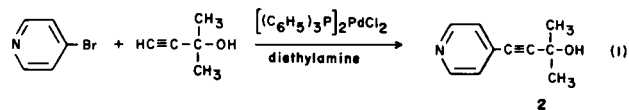
2-Methyl-4-(4-pyridyl)-3-butyne-2-ol (**2**) was prepared in 70% yield by the reaction of 4-bromopyridine with 2-methyl-3-butyne-2-ol in diethylamine in the presence of bis(triphenylphosphine)palladium(II) chloride and copper(I) iodide. Removal of the protective group in **2** by refluxing with sodium hydroxide in toluene yields (90%) 4-ethynylpyridine (**3**). Oxidative coupling of **3** in pyridine by dioxygen in the presence of copper(I) chloride produces a 92% yield of 1,4-bis(4-pyridyl)butadiyne.

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In the course of our studies [1,2] of intramolecular electron transfer between transition metal ions mediated by aromatic nitrogen heterocycles, we became interested in the effect of the distance [3] between the metal centers on the free energy of activation for electron transfer. Most of the bridging ligands utilized so far contain two pyridine rings connected by a backbone of carbon atoms. To ensure that the electron transfer takes place through the ligand [2] it is necessary that the backbone connecting the pyridine rings be rigid and conjugated. Therefore, it was decided to synthesize the new compound **1** which provides a distance of approximately 1.5 nm between first row transition



metal ions. In addition, the ligand is important in extending studies of coupling [4] between transition metal ions in mixed valence compounds. Moreover, the methylated analogue of compound **1** is a viologen and thus belongs to a class of compounds very useful in studies of solar energy storage [5].



The synthesis of intermediate **2**, 4-ethynylpyridine, has been described in the literature [6,7,8], but the methods are cumbersome and the overall yields reported are low (3.9% starting from 4-acetylpyridine, [6] 5% from 4-aminopyridine [7] and 29% from 4-vinylpyridine hydrochlor-

ide [8]) and insufficient for our purposes. A much higher yield (70%) was obtained by applying the convenient method developed by Ames, Bull and Takundwa for the synthesis of ethynyl-*N*-heteroarenes [9]. This involves the condensation of aryl halides with 2,2-dimethyl-3-butyne-2-ol, a protected acetylene, (which is commercially available) in the presence of bis(triphenylphosphine)palladium(II) dichloride and copper(I) iodide. The removal of the protecting group (as acetone) is accomplished by refluxing with sodium hydroxide in toluene, eq 2.

The desired ligand is then synthesized by oxidative coupling of the alkyne: its solution in pyridine is shaken in oxygen in the presence of copper(I) chloride (Eglinton reaction).

The purified product consists of very thin, colorless, shiny plates; it is very soluble in chloroform, fairly soluble in ether, methanol and acetone, insoluble in water. Proof of the composition and structure of the compound is based on analytical and spectroscopic data reported in detail below.

## EXPERIMENTAL

Diethylamine (Aldrich) and pyridine (Fisher) were dried over potassium hydroxide and distilled before use. Dry toluene (Fisher) was purified by distillation. 4-Bromopyridine hydrochloride (Aldrich), 2,2-dimethyl-3-butyne-2-ol (Aldrich), copper(I) iodide (Fisher) and copper(I) chloride (Fisher) were used as received. Bis(triphenylphosphine)palladium(II) dichloride was prepared using the literature method [10]. Visible and ultraviolet spectra were obtained using a Cary 118 spectrophotometer. Infrared spectra were obtained using a 727B Perkin Elmer spectrophotometer. The <sup>1</sup>H-nmr spectra were obtained on a Varian EM-360 instrument. The mass spectrum was obtained using a Hewlett-Packard 5980A mass spectrometer, preceded by a Hewlett-Packard 4710A gas chromatograph. The elemental analysis was performed by Galbraith Laboratories, Inc., Tennessee.

### 2-Methyl-4-(4-pyridyl)-3-butyne-2-ol (**2**).

Bis(triphenylphosphine)palladium(II) dichloride (0.35 g) and copper(I) iodide (50 mg) were added successively to 4-bromopyridine hydrochloride (9.7 g, 0.05 mole) and 2-methyl-3-butyne-2-ol (5 g, 0.06 mole) in diethylamine (100 ml) under nitrogen at room temperature. The mixture was stirred under nitrogen for 3 hours and the diethylamine was then evaporated under reduced pressure. Water was added and the organic product was extracted with ether. The palladium salts were eliminated by passing

the ether extract through a short column of alumina (neutral, activity I). Crystallization of the crude product from ethyl acetate/petroleum ether gave colorless crystals of 2-methyl-4-(4-pyridyl)-3-butyn-2-ol, yield 6.8 g (84%), mp 111-112° (uncorrected), lit [7] mp 111.5-112.5°; ir (chloroform):  $\text{cm}^{-1}$  2240 (C≡C) (shoulder at 2250), 3600 (OH) broad band of hydrogen bond with maximum at 3210.

#### 4-Ethynylpyridine (3).

A solution of 2 (4 g) in toluene (120 ml) was heated under reflux with sodium hydroxide (0.8 g) for 2 hours. The reaction mixture was filtered and the solvent was quickly evaporated in a large crystallization dish. The crude product was purified by sublimation (15 torr and 70°), yielding white crystals of 4-ethynylpyridine, yield 2.3 g (90%), mp 95-96° (uncorrected), lit [6] 96-96.5°; ir (carbon tetrachloride):  $\text{cm}^{-1}$  2125 (C≡C), 3310 (C≡CH); nmr (deuteriochloroform):  $\delta$  3.34 (C≡CH), 7.28 (2H $\alpha$ ), 8.50 (2H $\beta$ ), J = 6 Hz.

#### 1,4-Bis(4-pyridyl)butadiyne (1).

Copper(I) chloride (0.2 g) was added to a solution of 3 (2.6 g) in pyridine (50 ml) and the mixture was shaken in oxygen for 45 minutes. A crystalline precipitate appeared after 10 minutes. The reaction mixture was poured into 500 ml of water. The precipitate was filtered, washed with water and dried. Crystallization from carbon tetrachloride gave colorless plates of 1,4-bis(4-pyridyl)butadiyne, yield, 2.4 g (92%), mp 203-205° (uncorrected); ir (chloroform):  $\text{cm}^{-1}$  2165 and 2230 (C≡C); nmr (deuteriochloroform):  $\delta$  ppm 7.25 (2H $\beta$ ), 8.45 (2H $\alpha$ ); uv (methanol): max (log  $\epsilon$ ) 323 (4.39), 302 (4.45), 285 (4.35), 268 (4.18), 255 (4.49), 244 (4.51);

ms: m/e (relative intensity), 205 (15), M<sup>+</sup> 204 (100), 203 (10), 177 (11), 164 (6), 176 (10), 151 (12), 150 (10), 124 (5), 123 (5), 122 (5), 100 (5), 99 (5), 98 (13), 75 (5), 74 (6).

Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>: C, 82.33; H, 3.95; N, 13.72. Found: C, 82.41; H, 4.01; N, 13.74.

#### Acknowledgement.

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