495-71-6; **6e**, 134179-54-7; **6f**, 134179-55-8; **7a**, 134179-56-9; **7b**, 114815-06-4; **7c**, 134179-57-0; **7d**, 36159-76-9; **8**, 134179-58-1; **9**, 627-63-4; **10**, 114914-88-4; **11**, 114914-89-5; **12**, 102454-96-6; **13**, 134179-59-2.

Synthesis of 4′-Vinyl-2,2′:6′,2″-terpyridine

Kevin T. Potts* and Dilip Konwar

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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In several recent papers, we described the synthesis of 4′-vinyl-2,2′:6′,2″-terpyridine,[1] its homo- and copolymerization behavior,[2] and the electropolymerization of its transition-metal coordination complexes in chemically modified electrode studies.[1,3] Interest in the coordination chemistry of vinyl-substituted bipyridines (bpy) and terpyridines (terpy) continues unabated, with applications in polymer chemistry,[2,4] chemically modified electrodes,[5] and in solar energy conversion.[6] Synthetic sequences developed[1,5a,7] to date for the introduction of a vinyl substituent into ligands of this type are often relatively cumbersome, utilizing multistep reactions with accompanying low overall yields. By applying a combination of triflate, vinyltin, and Pd^0 chemistry,[8] we have resolved this problem in the terpyridine series, and a convenient synthesis of 4′-vinylterpy from ethyl 2-pyridinecarboxylate in a reasonable overall yield is described in this paper.

The use of Pd-catalyzed reactions in the formation of C–C bonds has been shown in recent years to provide an excellent alternative to more classical bond-formation reactions.[8a-f] The recent report that trifluoromethanesulfonates (triflates) undergo palladium-catalyzed coupling with organostannanes with the formation of a new C–C bond and the elimination of the triflate group,[8f] especially the palladium-catalyzed coupling of 2-quinolyl triflate with 5-(trimethylstannyl)-1,3-benzodioxole to afford[9] dubamine (79%), suggested this present application. The overall reaction sequence utilized in our synthesis is shown in Figure 1.

The requisite 2,6-di-2-pyridyl-4(1*H*)-pyridone (**3**) was prepared in two ways. 2,6-Di-2-pyridyl-4-(methylsulfonyl)pyridine (**2**), obtained from the corresponding methylthio compound **1** by peracid oxidation,[10] was hydrolyzed with 20% aqueous potassium hydroxide in dimethoxyethane with a catalytic amount of dibenzo-18-crown-6. An alternative procedure (80% yield) involved the reaction of 1,5-di-2-pyridylpentane-1,3,5-trione (**4**) with hot ammonium acetate, the trione itself being obtained (80% yield) from the Claisen condensation of ethyl 2-pyridinecarboxylate and acetone.[11] The triflate **5** was readily prepared (76% yield) from **3** and triflic anhydride in the presence of pyridine. Reaction of the triflate with vinyltributyltin using the general procedure described by Stille[9] gave 4′-vinyl-2,2′:6′,2″-terpyridine in up to 50% yield. However, use of the preformed catalyst bis(triphenylphosphine)palladium dichloride in DMF/Et$_3$N solution under the reaction conditions described in the Experimental Section increased the yield of the 4′-vinylterpy to 86%. An interesting feature of these experimental conditions was the absence of added lithium chloride in the reaction mixture. Others have also observed that added chloride is not necessary for vinylation to occur with aryl halides,[12,13] vinyl triflates,[14] or with pyrimidyl triflates.[15] An alternative reaction procedure for this type of coupling described by Chen[12] resulted in slightly reduced yields of the vinyl compound.

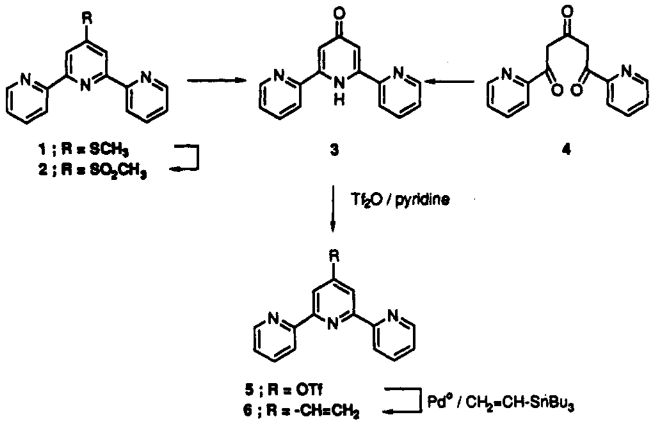

Figure 1. Reaction sequence for the formation of 4′-vinyl-2,2′:6′,2″-terpyridine.

Experimental Section[16]

2,6-Di-2-pyridyl-4(1*H*)-pyridone (3). A: From 2,6-Di-2-pyridyl-4-(methylsulfonyl)pyridine (2). A mixture of the (methylsulfonyl)pyridine **2** (0.30 g, 0.096 mmol) and aqueous potassium hydroxide (20 mL of 20% solution), DME (20 mL), and a catalytic amount of dibenzo-18-crown-6 (50 mg) was refluxed for 48 h. The resultant homogeneous mixture was cooled to room temperature and diluted with water. The organic layer was distilled off and the residual solution neutralized with acetic acid, giving a white solid (mp >400 °C) that was removed. The filtrate was extracted with CHCl$_3$, and after drying (Na$_2$SO$_4$) and evaporation of the extract, a residue containing starting material and pyridone was obtained. This residue was boiled in water while ethanol was added slowly until homogeneity was achieved and, on cooling of the solution, the starting material separated. Reduction of the filtrate to a small volume resulted in white microneedles of the pyridone separating from solution: 0.05 g (32 %), mp 165 °C; IR (KBr) ν_{NH} 3300, ν_{CO} 1630 cm^{-1}; ^{1}H NMR

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0022-3263/91/1956-4815$02.50/0

($CDCl_3$) δ 8.90–7.20 (m, 10 H, aromatic and 2-pyridine H), 7.11 (s, 1 H, NH); mass spectrum *m*/*z* (relative intensity) (EI) M^+ 249 (100).

B: From 1,5-Di-2-pyridylpentane-1,3,5-trione (4). The procedure described in the following text for the preparation of 4 is a significant improvement over that reported[11] in the literature. A solution of acetone (1.8 mL, 25 mmol) and ethyl 2-pyridinecarboxylate (10.1 mL, 75 mmol) in dry THF (50 mL) was added dropwise to a refluxing suspension of sodium hydride (95%, 1.9 g, 75 mmol) in dry THF (50 mL) in a nitrogen atmosphere over 4 h. After an additional reflux (2 h), the THF was removed in vacuo and the remaining orange paste carefully treated with water (100 mL). The resultant orange solution was filtered through Celite and the pH of the filtrate adjusted to pH 7 by the dropwise addition of 5% acetic acid. The resultant yellow solid was collected, washed with water, and dried. After recrystallization from 95% ethanol, the triketone was obtained as small, yellow needles: 5.4 g (80%), mp 105 °C (lit.[10] mp 105 °C); IR (KBr) ν_{CO} 1611, 1560 cm^{-1}; mass spectrum *m*/*z* (relative intensity) (CI) (M + 1) 269 (100). Conversion of this triketone into the pyridone 3 was carried out using the method described in the literature.[11]

4′-[[(Trifluoromethyl)sulfonyl]oxy]-2,2′:6′,2″-terpyridine (5). A solution of 2,6-di-2-pyridyl-4(1*H*)-pyridone (498 mg, 2 mmol) in dry pyridine (5 mL) was treated slowly at 0 °C with trifluoromethanesulfonic anhydride (594 mg, 2 mmol). The resulting mixture was stirred at 0 °C (30 min), allowed to warm to room temperature (25 °C), and kept at this temperature for 48 h. It was then poured into ice–water (50 g) and stirred for 0.5 h. The light-brown solid was separated, washed with cold water (50 mL), and, after drying, dissolved in hexane (15 mL), and the insoluble portion was filtered off. Concentration of the mother liquor to ca. 5 mL and cooling gave colorless, irregular prisms of the triflate: 0.53 g (70%); mp 108 °C; IR (KBr) 1575, 1435–1405, 1245–1200, 1135, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–8.8 (m, 10 H, aromatic protons); mass spectrum (CI) *m*/*z* (relative intensity) $(M + 1)^+$ 382 (100), 250 (30), 234 (16). Anal. Calcd for $C_{16}H_{10}N_3O_3SF_3$: C, 50.39; H, 2.64; N, 11.02. Found: C, 50.30; H, 2.47; N, 10.91.

Preparation of 4′-Vinyl-2,2′:6′,2″-terpyridine (6). A mixture of 4′-[[(trifluoromethyl)sulfonyl]oxy]-2,2′:6′,2″-terpyridine (1.91 g, 5 mmol), vinyltributyltin (2.22 g, 7 mmol), NEt_3 (3 mL, 22 mmol), and bis(triphenylphosphine)palladium dichloride (100 mg, 0.14 mmol) in DMF (15 mL) was stirred at 90 °C for 4 h under dry nitrogen. The reaction mixture was then diluted with ice–water (100 mL), stirred for 1 h, and filtered. The light-yellow solid was washed several times with water and dried. The crude product was dissolved in diethyl ether (100 mL) and the insoluble material removed by filtration. Evaporation of the ether under reduced pressure resulted in a pale-yellow solid that was chromatographed on neutral alumina using a 9:1 hexane/ethyl acetate mixture as the eluting solvent. Removal of the solvent under reduced pressure yielded 4′-vinylterpyridine as colorless, irregular prisms: 1.1 g (86%), mp 90–91 °C (lit.[1] mp 89–91 °C); IR (KBr) 1600–1550, 1465, 1380, 990, 929, 790, 745 cm^{-1}; ^1H NMR ($CDCl_3$; 200 MHz) δ 8.74–7.27 (m, 10 H, aromatic), 6.89 (dd, 1 H, H_b, J_{Hb-Ha} = 10.9 Hz, $J_{Hb-Ha'}$ = 17.6 Hz), 6.22 (d, 1 H, H_a', $J_{Ha'-Hb}$ = 17.6 Hz), 5.56 (d, 1 H, H_a, J_{Ha-Hb} = 10.9 Hz); mass spectrum (CI) *m*/*z* (relative intensity) $(M + 1)^+$ 260 (100). Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.73; H, 5.06; N, 16.21. Found: C, 78.02; H, 5.15; N, 15.57.

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Additions and Corrections

Vol. 54, 1989

Mouhsine Lourak, Régis Vanderesse, Yves Fort, and Paul Caubère*. Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 32. NiCRAL's as Very Efficient Agents in Promoting Cross-Coupling of Aryl Halides.

Page 4847, column 1, paragraph 7. *t*-AmONa (20 mmol) should read *t*-AmOH (20 mmol).

Vol. 55, 1990

A. Srikrishna* and P. Hemamalini. Radical Cyclization Strategies to Bridged Systems. Synthesis of Bicyclo[3.2.1]octan-3-ones from (*S*)-Carvone.

Page 4884, Table I, column 6 ($[\alpha]_D$), should read as follows:

endo	exo
-51.8	-26.0
-23.9	-10.7
-39.1	-10.7
-30.7	-12.4
-32.5	-12.7
-14.1	-5.6
-24.6	-0.3

Vol. 56, 1991

Jeffrey C. Bottaro, Paul E. Penwell, and Robert J. Schmitt*. Improved Synthesis of Cubane-1,2,4,7-tetracarboxylic Acid.

Page 1306, columns 1 and 2, compounds 1 and 2 in Scheme I and Table I should be drawn as follows:

Scheme I

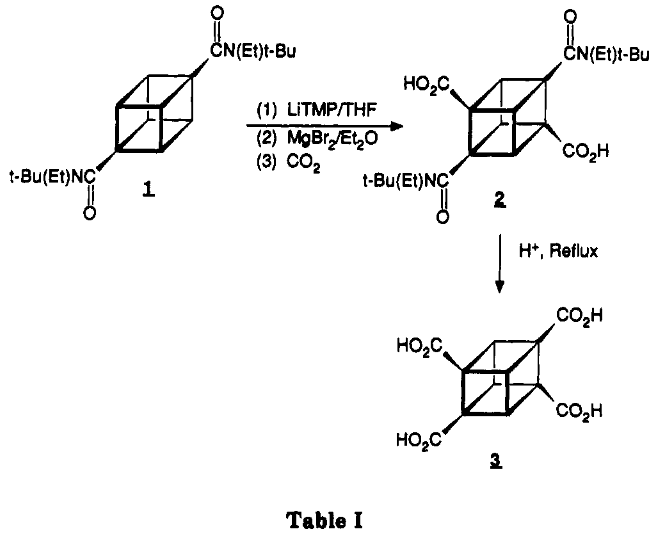

Table I