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Suzuki Cross-coupling Method to Prepare 4,4"-Diamino-*p*-terphenyl

Matthew C. Davis

Chemistry & Materials Division, Michelson Laboratory, Naval Air Warfare Center, China Lake, California, USA

Abstract: The synthesis of 4,4"-dinitro-*p*-terphenyl is accomplished by double Suzuki cross-coupling. The product was reduced catalytically to give 4,4"-diamino-*p*-terphenyl in 75% overall yield.

Keywords: Diamino, dinitro, palladium, Suzuki reaction, terphenyl

As part of a project to prepare redox active polymers, 4,4''-diamino-*p*terphenyl was required. The compound had been previously synthesized and studied by Hammond and Pavlopoulos as a laser dye.^[1,2] The compound is available from Lancaster Synthesis (Windham, NH) but is too expensive for our purposes; 2004–2005 catalog #5403, 5 g/\$235 USD. The first step in Hammond and Pavlopoulos's synthesis was the mixed-acid nitration of commercially available *para*-terphenyl. The 4,4''-dinitro-*p*-terphenyl was conveniently isolated in pure form directly from the cooled reaction mixture in 32% yield. The dinitro compound was then reduced with tin and acid in 76% yield, giving the product in 24% overall yield from *para*-terphenyl. An alternative method was sought to avoid the low-yielding and nonselective nitration and to find a reduction procedure that does not require stoichiometric heavy metals.

Al-Masri et al. previously reported that phenyldiboronic acids undergo double Suzuki cross-coupling with nitroarylbromides to provide

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Address correspondence to Matthew C. Davis, Chemistry & Materials Division (Code 498220D), Michelson Laboratory, Naval Air Warfare Center, China Lake, California, USA. E-mail: matthew.davis@navy.mil

dinitro-*p*-terphenylenes.^[3] We adopted this strategy with similarly excellent results (Scheme 1). Coupling between compounds 1 and 2 gave the dinitro 3, which precipitated from the reaction mixture. The residual palladium contained in 3 was removed by recrystallization from DMF, giving pure product in 76% yield. The subsequent catalytic reduction of 3 to 4 proceeded without complication in 99% yield.

In conclusion, the synthesis of 4,4''-diamino-*p*-terphenyl has been updated. This new method employs a double Suzuki cross-coupling followed by catalytic reduction. The product is provided in 75% overall yield from commercially available 1,4-phenylenebisboronic acid.

EXPERIMENTAL

Melting points were collected on an electrothermal capillary melting-point apparatus and are not corrected. NMR spectra were obtained on a Bruker AC-200 spectrometer (¹H at 200 MHz, ¹³C at 50 MHz) and are referenced to solvent or tetramethylsilane. The following reagents were purchased from Aldrich Chemical Co. (Milwaukee) and used as received: 1-bromo-4-nitrobenzene 1, 99% tetrahydrofuran (inhibited with 250 ppm BHT), 1,4-phenylenebisboronic acid 2, and 99% tetrakis(triphenylphosphine)palladium(0). The 5% palladium on carbon catalyst was purchased from Lancaster Synthesis (Windham, NH). All other reagents were obtained commercially and used as received.

4,4"-Dinitro-*p*-terphenyl (3)

A 1-L, round-bottomed flask equipped with magnetic stir bar was charged with 7.6 g of 1,4-phenylenebisboronic acid 1 (0.046 mol, 1 equiv), 18.55 g



Scheme 1. Reagents and conditions: a) Pd(PPh₃)₄, K₂CO₃, THF, H₂O, reflux; b) Pd/C, THF, H₂, 40 psig.

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of 1-bromo-4-nitrobenzene **2** (0.092 mol, 2 equiv), 400 mL of THF, and 92 mL of 2 M K₂CO₃ (0.184 mol, 4 equiv). A reflux condenser and N₂ bubbler were attached, and the mixture was heated gently to dissolve all the solids. Tetra-kis(triphenylphosphine)palladium(0) (600 mg) was added in one portion, and the mixture was refluxed for 18 h. The product precipitated from the reaction mixture as the reaction proceeded. After this time, the mixture was cooled to rt, and 200 mL of H₂O was added. The solids were collected on a medium-porosity glass frit and washed with 200 mL of H₂O. The solids were transferred to a 500 mL beaker and recrystallized from 250 mL of DMF. The bright yellow powder was collected on a medium-porosity glass frit, washed with EtOH, and air dried on the frit (11.2 g, 76%). Mp 270–272°C (lit.^[2] 274–275°C). $\delta_{\rm H}$ (DMSO- d_6): 8.35 (d, J = 8.8 Hz, 4H), 8.07 (d, J = 9.0 Hz, 4H), 7.99 (s, 4H); $\delta_{\rm C}$ (DMSO- d_6 at 125°C): 146.70, 145.18, 137.86, 127.38, 127.26, 123.37. Anal. calcd. for C₁₈H₁₂N₂O₄: C, 67.5; H, 3.78; N, 8.75. Found: C, 67.51; H, 3.62; N, 8.64.

4,4"-Diamino-*p*-terphenyl (4)

A mixture of 26.8 g of 3, 1-L of THF (containing 250 ppm BHT), and 2 g of 5% Pd on carbon catalyst were shaken on a Parr[®] hydrogenator for 18 h (40 psig). After 1 h, the reaction mixture appeared orange and opaque. After 18 h, the mixture was colorless. To the reaction mixture were added 500 mL of hexanes, and then the mixture was filtered through diatomaceous earth on a coarse glass frit. The addition of hexanes ensured complete removal of the catalyst by a single filtration; otherwise a small amount of catalyst was inevitably entrained. The colorless filtrate was rotary evaporated, leaving a white solid. The material was placed under vacuum to remove residual solvent (rt, 1 Torr) and was pure by NMR. An analytical sample was made by recrystallization from MeCN, providing the title compound as small colorless plates. Mp 240-241°C with decomposition (lit.^[4] 248-253°C and lit.^[5] 240°C). The product can also be recrystallized from 1,4-dioxane or toluene. $\delta_{\rm H}$ (DMSO- d_6): 7.56 (s, 4H), 7.41 (d, J = 8.3 Hz, 4H), 6.69 (d, J = 8.3 Hz, 4H); $\delta_{\rm C}$ (DMSO- d_6): 148.19, 137.96, 127.24, 126.89, 125.63, 114.36. Anal. calcd. for C₁₈H₁₄N₂: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.75; H, 6.21; N, 10.60.

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