A New Bipyrrole Coupling Reaction

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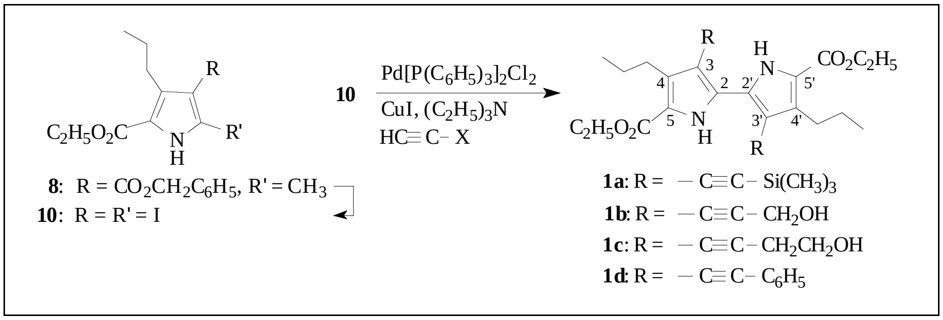
Received July 24, 2006

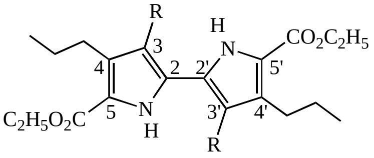


Pyrrole **8** was converted to **10** in 4 steps, and **10** was coupled directly to bipyrroles **1** in a Sonogashira reaction, respectively at the 3,3′ positions.

J. Heterocyclic Chem., **44**, 739 (2007).

INTRODUCTION

Bipyrroles first appeared in *Chemical Abstracts* in 1914, with ~550 citations to the present. In contrast, there have been ~70,000 citations for biphenyl since 1904. Among the five possible isomers of bipyrrole, 2,2′-bipyrroles appear in the literature more frequently than any other, although they generally appear late and infrequently in the first half of the twentieth century. Successful directed syntheses of bipyrroles began to appear in the 1950s, most often by an Ullmann-type radical recombination coupling of 2-iodopyrroles [1-4] – although other coupling methods, e.g., $FeCl_3$ with α-H pyrroles, have been used [1,5]. In the following, we show a new method for coupling 2-iodopyrroles that also inserts acetylene groups at 3,3′ of the resultant bipyrrole.



1a: R = —C≡C—$Si(CH_3)_3$
1b: R = —C≡C—CH_2OH
1c: R = —C≡C—CH_2CH_2OH
1d: R = —C≡C—C_6H_5

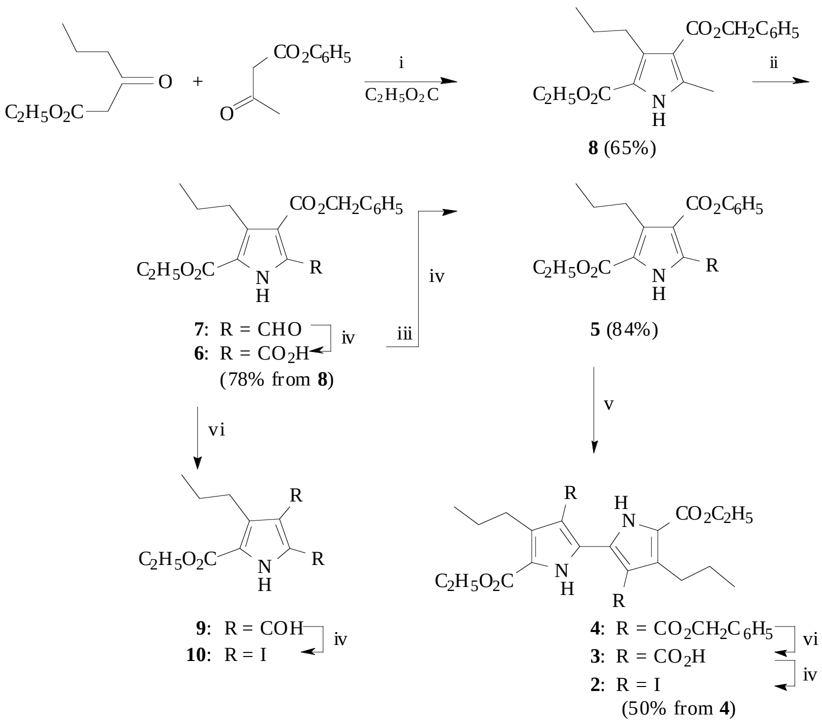
Figure 1. The target 3,3'-diacetylene-substituted 2,2'-bipyrroles of this work.

RESULTS AND DISCUSSION

The target bipyrroles were **1a**-**1d** (Figure 1), for which we had devised a stepwise procedure (Scheme 1) from pyrrole diester **8** that was synthesized by a Fischer-Knorr condensation between ethyl butyrylacetate and benzyl acetoacetate [6]. Two key steps were involved: Cu-catalyzed bipyrrole formation (to **4**) and a Sonogashira reaction [7-9] to replace the 3,3′-diodo groups of **2** with acetylene units that led to bipyrroles **1a**, **1b** and **1d** in overall yields of approximately 9%, 11% and 7%. The low overall yields were viewed as unattractive and led us to attempt to shorten the number of steps by going more directly from **6** to **2** via the 4,5-diiodopyrrole **10** (Scheme 1). Thus, **6** was converted with conc. H_2SO_4 smoothly to **9**, which provided **10** in 63% overall yield from **6** upon treatment of **9** with iodine and potassium iodide in aqueous bicarbonate. Attempted copper-catalyzed coupling reaction of **10** failed to give **2**, however, and no recognizable products were obtained. Realizing that the Sonogashira reaction conditions (absent the acetylene component) did not induce bipyrrole formation from either **5** or **10**, we attempted to convert **10** to its 5-iodo-4-acetylene derivative using trimethylsilylacetylene in a Sonogashira reaction. Surprisingly, the product obtained in high yield was bipyrrole **1a** and not the expected 5-iodo-3-trimethylsilylacetylene monopyrrole. This substitution-coupling reaction using other mono-substituted acetylenes (Scheme 1) led to good yields of **1c**-**1d**. Thus unexpectedly, we found a higher yield synthesis of **1a**, **1b**, **1c** and **1d**, with overall yields from **8** of 34%, 25% 30% and 19%, respectively.

The mechanism of formation of **1** from **10** is unclear. However, since the Sonogashira conditions absent the acetylene do not lead to bipyrrole formation, it seems reasonable to assume the first step involves replacing the 4-iodo of **10** by the acetylene component, and the 5-iodo-3-acetylene monopyrrole undergoes coupling to the bipyrrole. Because ethyl 5-iodo-3-ethyl-4-methyl-bipyrrole-2-carboxylate does not undergo coupling to a

Scheme 1 [a]



[a] Reagents and conditions: i, HONO on ethyl butyrylacetate, then Zn/CH_3CO_2H/Δ while benzyl acetoacetate is added; ii, $Br_2/SO_2Cl_2/CH_3CO_2H$; iii, $KMnO_4$/acetone; iv, I_2, KI, $NaHCO_3$; v, Cu/DMF; vi, conc. H_2SO_4; vii, $Pd[P(C_6H_5)_3]_2Cl_2/CuI/(C_2H_5)_3N$ + $HC{\equiv}C\text{-}Si(CH_3)_3$, $H\text{-}C{\equiv}C\text{-}CH_2OH$, $HC{\equiv}C\text{-}CH_2CH_2OH$ or $HC{\equiv}CC_6H_5$

bipyrrole under Sonogashira reaction conditions, it appears likely that the 4-acetylene group is necessary to facilitate the coupling, perhaps by complexing with the palladium reagent, thereby bringing it close to the 5-iodo reaction center for bipyrrole formation.

Interestingly, the reaction conditions that successfully provided a substituted bipyrrole from an α,β-diiodopyrrole failed to convert 1,2-diiodobenzene to a biphenyl and led only to disubstitution on the ring, as has been shown previously [7-9]. Thus, reaction of 1,2-diiodobenzene with trimethylsilylacetylene yielded only 1,2-bis(trimethyl(silylacetylenyl) benzene, and the product from phenylacetylene was 1,2-di(phenyl-acetylenyl) benzene. Apparently on the aromatic ring, the rate of biphenyl coupling of the supposed mono-acetylene adduct with an *ortho* iodine is slow compared to substitution with the second acetylene group.

EXPERIMENTAL

All nuclear magnetic resonance (nmr) spectra were obtained on a General Electric QE-300 or GN-300 at 300 MHz (proton) and 75 MHz (C-13), respectively, in deuteriochloroform unless otherwise indicated. Chemical shifts were reported in ppm referenced to the residual chloroform proton signal at 7.26 ppm and C-13 signal at 77.23 ppm unless otherwise noted. All GC-MS spectra were obtained from a Varian CP-3800 mass spectrometer. Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected. Combustion analyses was performed by Desert Analytics, Tuscon, AZ. Infrared spectra were recorded on a Perkin-Elmer FT-IR infrared spectrophotometer model SPECTRUM 2000. All ultraviolet-visible spectra were recorded on a Perkin-Elmer λ-12 spectrophotometer. Analytical thin layer chromatrography (tlc) was carried out on J.T. Baker silica gel IB-F plates (125 μm layer). For purification, radial chromatography was carried out on Merck silica gel PF_{254} with calcium sulfate binder, preparative layer grade. Flash column chromatography was carried out using silica gel, 60-200 mesh (M. Woelm, Eschwege). All solvents were reagent grade obtained from Fisher or Acros, as was the ethyl butyrylacetate. Deuterated chloroform, dichloro-methane and dimethylsulfoxide were from Cambridge Isotope Laboratories. Trimethylsilylacetylene, propargyl alcohol, 3-butyn-1-ol and phenylacetylene were from GFS Chemicals. Copper(I) iodide (Cu_2I_2, 98%, stock #26110, lot #060674 was from Alfa Products. Copper powder (99% for organic synthesis, batch #16920AB), Palladium(II) acetate and bis(triphenyl-phosphine) palladium(II) chloride were from Sigma Aldrich.

Ethyl 4-carbobenzyloxy-5-methyl-3-*n*-propyl-1*H*-pyrrole-2-carboxylate (**8**). A two liter three-necked round bottom flask was equipped with a paddle stirrer, a dropping funnel and a thermometer. Ethyl butyrylacetate (50.0 g, 0.316 moles) was added to 240 ml of glacial acetic acid and cooled in an ice bath to 5°C. A solution of sodium nitrite (24.4 g, 0.32 moles) in water (60 ml) was added dropwise over 1 hour. The solution was then allowed to warm to room temperature and was stirred for 4 hours. Benzyl acetoacetate (60.5 g, 0.315 moles) was added all at once to the solution, followed by portions of zinc dust (42 g, 0.64 g-atom total) with stirring. As the zinc was added, the temperature of the flask slowly rose to 70°C. After the addition was complete, the solution was kept between 65°C and 75°C for 1.5 hours using a hot water bath. The solution was then poured into 2 liters of ice water and stirred magnetically for 30 minutes. The precipitate was collected by vacuum filtration, washed with water, and dissolved in dichloromethane. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from ethanol to give 62.2 g, 0.319 mol (65% yield) of the product as a colorless solid. It had mp 80-81°C; GC-MS (m/z): 329 [M$^{+\bullet}$], 267, 238, 194, 192, 166; ir (KBr): 3295, 2960, 2343, 1700, 1666, 1436, 1278, 1264, 1194, 1085, 698 cm^{-1}; H nmr: 0.86 (t, 3H, J = 7.0 Hz), 1.36 (t, 3H, J = 7.0 Hz), 1.52 (m, 2H), 2.50 (s, 3H), 3.00 (t, 2H, J = 8.0 Hz), 4.32 (q, 2H, J = 7.0 Hz), 5.28 (s, 2H), 7.37 (m, 5H), 8.98 (brs, 1H) ppm; C-13 nmr: 14.0, 14.3, 14.4, 24.5, 27.6, 60.3, 65.6, 112.6, 117.8, 128.0, 128.3, 128.5, 135.9, 136.5, 139.5, 161.8, 165.0 ppm. *Anal.* Calcd for $C_{19}H_{23}NO_4$ (329.4): C, 69.30; H, 6.99; N, 4.26. Found: C, 69.15; H, 7.16; N, 4.41.

3-Benzyloxycarbonyl-5-ethoxycarbonyl-4-propyl-1*H*-pyrrole-2-carboxylic acid (**6**). Mixed diester **8** (24.6 g, 74.8 mmoles) was added to 100 ml of glacial acetic acid in a three-neck round bottom flask. The contents were stirred mechanically and cooled to 10°C in an ice bath. Bromine (3.7 ml, 74 mmoles) was added to the solution all at once. Freshly distilled sulfuryl chloride (18.9 ml, 226 mmoles) was then added dropwise over 1.5 hours. During the addition, care was used to ensure that the mixture was stirred vigorously (the contents of the flask will precipitate massively during addition). After all of the sulfuryl chloride has been added, the solution was allowed to reach room temperature and was stirred for 4.5 hours. Water (40 ml) was then added dropwise. After the addition was complete, the solution was heated on a hot water bath at 60°C for 30 minutes. The solution was then poured into one liter of ice water and stirred. The precipitate was collected by vacuum filtration and washed with water. The precipitate was dissolved in saturated aqueous sodium bicarbonate. The undissolved aldehyde (**7**) was collected by vacuum filtration and the filtrate was acidified with dilute hydrochloric acid. The resulting precipitate was collected by vacuum filtration, washed with water, and dried. Acid (**6**) was recrystallized from 2-propanol to afford 11.25 g, 43.4 mmol. Aldehyde (**7**) (the side product from this reaction) was dissolved in 150 ml of reagent acetone and a solution of potassium permanganate (5 g in 200 ml of acetone/water (1:1)) was added over 1 hours. After 10 hours of stirring at room temperature, the purple solution was poured into 250 ml of 10% aqueous $NaHSO_3$, and the mixture was extracted with chloroform (3 x 200 ml). The combined chloroform extracts were washed with water (2 x 200 ml) and with saturated aqueous sodium chloride (1 x 200 ml, dried over sodium sulfate, filtered, and evaporated, leaving crude resulting acid which was also recrystallized from 2-propanol. The combined yield of 3-benzyloxy-carbonyl-5-ethoxy-carbonyl-4-propyl-1*H*-pyrrole-2-carboxylic acid (**6**) was 21.3 g, 59.4 mmol, (79%). It had mp 133-134°C; ir (KBr): 3261, 1737, 1695, 1492, 1443, 1269, 1011, 764 cm^{-1}; H nmr (dimethylsulfoxide-d$_6$): 0.76 (t, 3H, J = 7.0 Hz), 1.39 (t, 3H, J = 7.0 Hz), 1.40 (m, 2H), 2.97 (t, 2H, J = 6.8 Hz), 4.37 (q, 2H, J = 7.0 Hz), 5.43 (s, 2H), 7.44 (m, 5H), 10.30 (brs, 1H) ppm; C-13 nmr (dimethylsulfoxide-d$_6$): 13.6, 14.0, 23.8, 26.4, 60.1, 66.1, 118.3, 120.9, 127.2, 128.0, 128.1, 128.3, 131.7, 135.8, 159.9, 160.9, 164.3 ppm. *Anal.* Calcd for $C_{19}H_{21}NO_6$ (359.4): C, 63.51; H, 5.85; N, 3.90. Found: C, 63.60; H, 5.85; N, 3.86.

Ethyl 4-benzyloxycarbonyl-5-iodo-3-propyl-1*H*-pyrrole-2-carboxylate (**5**). In a 600 ml beaker, 10.2 g (28.4 mmoles) of 3-benzyloxycarbonyl-5-ethoxycarbonyl-4-propyl-1*H*-pyrrole -2-carboxylic acid (**6**) was dissolved in 100 ml of hot ethanol. Sodium bicarbonate (8.66 g) and 100 ml of water were added carefully to the mixture. The mixture was then heated to 70°C on a hot plate. Potassium iodide (13.8 g) and iodine (8.01 g) were dissolved in 85 ml of water. The iodine mixture was then added drop wise at such a rate as to minimize the gas evolution. The endpoint was slightly purple colored. The contents of the flask were cooled to 50°C and the precipitate was collected by vacuum filtration. The precipitate was dissolved in chloroform and dried over sodium sulfate. The sodium sulfate was removed by gravity filtration, and the solvent was evaporated under reduced pressure. The product was recrystallized from ethanol to give 9.76 g (78%) as colorless needles with mp 154-155°C; H nmr: 0.83 (3H, t, J = 7 Hz), 1.37 (3H, t, J = 7 Hz), 1.49 (2H, sex., J = 8 Hz), 3.00 (2H, t, J = 8 Hz), 4.33 (2H, q, J = 7 Hz), 5.31 (2H, s), 7.41 (5H, m), and 9.26 (1H, br.s) ppm. C-13 nmr: 13.9, 14.3, 24.4, 27.7, 60.8, 66.2, 124.9, 128.2, 128.5, 128.6, 138.8 (135.76), 135.8 (135.5), 160.3, and 163.2 ppm. *Anal.* Calcd for $C_{18}H_{20}NIO_4$ (441.3): C, 49.00; H, 4.57; N, 3.17. Found: C, 49.48; H, 4.71; N, 3.21.

Diethyl 3,3′-bis(benzyloxycarbonyl)-4,4′-dipropyl-2,2′-bipyrrole-3,3′,5,5′-tetracarboxylate (**4**). In a 100-ml round bottom flask, 9.66 g 21.9 mmoles) of 4-benzyl 2-ethyl 5-iodo-3-propyl-pyrrole-2,4-dicarboxylate (**5**) was dissolved in 60 ml of dry dimethylformamide. Activated copper (9.0 g) [10] was added to the flask, which was then stoppered, covered with aluminum foil, and stirred for 15 h. Chloroform (100 ml) was then added to the mixture, and the unreacted copper was removed by vacuum filtration and rinsed with 100 ml of chloroform. The combined organic solutions were washed with 1 N aqueous hydrochloric acid (2 x 60 ml), brine (60 ml), and saturated aqueous sodium bicarbonate (60 ml). The solution was then dried over sodium sulfate, removed from the mixture by gravity filtration and evaporated under reduced pressure to yield a solid that was recrystallized from ethanol to give 3.78 g (55%) of **4** as colorless needles. It had mp 165-166°C; H nmr: 0.72 (6H, t, J = 7 Hz), 1.42 (6H, t, J = 7 Hz), 1.43 (4H, sex., J = 8 Hz), 3.00 (4H, t, J = 8 Hz), 5.37 (4H, q, J = 7 Hz), 7.40 (10H, m), and 14.2 (2H, br. s) ppm. C-13 nmr: 13.9, 14.3, 24.7, 28.0, 60.4, 67.5, 112.8, 119.8, 128.5, 128.6, 129.1, 129.9, 135.3, 136.6, 160.8 and 168.0 ppm. *Anal.* Calcd. $C_{36}H_{40}N_2O_8$ (628.7): C, 68.79; H, 6.37; N, 4.46. Found: C, 68.83; H, 6.66; N, 4.54.

Diethyl 3,3′-diiodo-4,4′-dipropyl-2,2′-bipyrrole-5,5′-dicarboxylate (**2**). Tetraester **4** (0.97 g) was carefully added in portions to 10 ml of concentrated sulfuric acid at 50°C and stirred for 5 minutes. The solution was then poured into 200 ml of ice water and was stirred vigorously for 10 minutes. The precipitate (0.70 g), collected by vacuum filtration, was used without further purification. In a 50-ml beaker, 0.70 g of crude 5,5′-diethoxycarbonyl-4,4′-dipropyl-2,2′-bipyrrole-3,3′-dicarboxylic acid (**3**) was dissolved in 10 ml hot ethanol. Sodium bicarbonate (0.7 g) and 10 ml of water were carefully added to the mixture. The mixture was then heated to 65°C on a hot plate. Potassium iodide (2.20 g) and iodine (1.26 g) were dissolved in 15 ml of water and used to treat the diacid as described for **5** above. The product (**2**) was recrystallized from 2-propanol-water to give 0.44 g (47% from **4** as colorless needles with mp 151-152°C, H nmr: 1.00 (6H, t, J = 7 Hz), 1.39 (6H, t, J = 7 Hz), 1.57 (4H, m), 2.75 (4H, t, J = 8 Hz) 4.36 (4H, q, J = 7 Hz) and 10.06 (2H, br. s) ppm; C-13 nmr: 13.9, 14.3, 23.5, 30.1, 60.6, 69.3, 119.7, 126.0, 135.3 and 160.2 ppm. *Anal.* Calcd for $C_{20}H_{26}I_2N_2O_6{\cdot}H_2O$ (630.3): C, 38.11; H, 4.16; N, 4.44. Found: C, 38.14; H, 4.22 N, 4.49.

Ethyl 4,5-diiodo-3-propyl-1*H*-pyrrole-2-carboxylate (10). 3-Benzyloxycarbonyl-5-ethoxycarbonyl-4-propyl-2-carboxylic acid (**6**) (20 g, 55.65 mmoles) was carefully added in portions to 150 ml of concentrated sulfuric acid at 50°C and was stirred for 5 minutes. The solution was then poured into 1000 ml of ice water and was stirred vigorously for 10 minutes. The precipitate was then collected by vacuum filtration. The crude product was sensitive toward decarboxylation and was used in the next step without further purification. It had mp 134-135°C (dec.); ir (KBr): 3447, 3261, 2594, 1737, 1693, 1623, 1268, 1011, 811 cm^{-1}; H nmr (dimethylsulfoxide-d$_6$): 0.85 (t, 3H, J = 7.4 Hz), 1.27 (t, 3H, J = 7.2 Hz), 1.47 (m, 2H), 2.76 (t, 2H, J = 7.4 Hz), 4.24 (q, 2H, J = 7.2 Hz), 12.51 (s, 1H), 13.37 (s, 1H); C-13 nmr (dimethylsulfoxide-d$_6$): 13.8, 14.0, 23.8, 26.5, 60.2, 118.5, 121.4, 127.4, 133.4, 159.9, 101.0, 167.0.

In a 1000 ml beaker, 10 g (37.1 mmoles) of crude 5-ethoxycarbonyl-4-propyl-1*H*-pyrrole-2,3-dicarboxylic acid (**9**) was dissolved in 70 ml of hot ethanol. Sodium bicarbonate (31.2 g, 371 mmoles) in 200 ml of water was carefully, in portions added to the mixture. The mixture was then heated to 65°C on a hot plate. Potassium iodide (18.4 g, 111 mmoles) and iodine (22.6 g, 178 mmoles) were dissolved in 350 ml of water at 50-55°C. The iodine mixture was then added dropwise only as quickly as it was decolorized to minimize (CO_2) gas evolution. The endpoint was colored slightly purple. The contents of the flask were cooled to 50°C, and the precipitate was collected by vacuum filtration. Then it was dissolved in dichloromethane and dried over anhydrous sodium sulfate. The sodium sulfate was removed by vacuum filtration, and the solvent was evaporated under reduced pressure. The product was recrystallized from 2-propanol/water (50/50, by volume) to give 15.2 g, 35 mmoles of diiodide **10** (63% from (**6**)) as a white solid. It had mp 154-155°C; ir (KBr): 3245, 2978, 1694, 1669, 1422, 1264, 1231, 1182, 781 cm^{-1}; H nmr: 0.95 (t, 6H, J = 7.5 Hz), 1.38 (t, 6H, J = 7.0 Hz), 1.56 (m, 4H), 3.06 (t, 4H, J = 7.5 Hz), 4.34 (q, 4H, J = 7.0 Hz), 9.18 (brs, 2H) ppm; C-13 nmr: 14.1, 14.6, 23.7, 31.5, 60.9, 82.1, 84.2, 124.5, 136.6, 160.6 ppm. *Anal.* Calcd. for $C_{10}H_{13}I_2NO_2$ (433.0): C, 27.74; H, 3.03; N, 3.23. Found: C, 27.50; H, 2.74; N, 3.39.

Diethyl 3,3′-Bis(trimethylsilylethynyl)-4,4′-di-propyl-2,2′-bipyrrole-5,5′-dicarboxylate (**1a**). Diiodopyrrole **10** (0.3 g, 0.7 mmoles), bis(tri-phenylphosphine)palladium(II) dichloride (0.05 g, 0.07 mmoles), cuprous iodide (0.03 g, 0.14 mmoles) and (trimethylsilyl)acetylene (0.21 g, 0.3 ml, 2.1 mmoles) were dissolved in 15 ml of freshly distilled triethylamine. The mixture was heated at 60°C and stirred under nitrogen overnight. After cooling, the solvent was evaporated at reduced pressure, and the crude product was redissolved in dichloromethane then vacuum filtered through a pad of silica gel. The solvent was evaporated to yield product **1a**, which was purified by radial chromatography (CH_2Cl_2 eluent). The yield of (**1b**) was 0.27 g, 0.49 mmol (70%). It had mp 123-124°C; ir (KBr): 3248, 2958, 2164, 1676, 1456, 1263, 1105, 884 cm^{-1}; H nmr: 0.33 (s, 18H), 0.95 (t, 6H, J = 7.5 Hz), 1.37 (t, 6H, J = 7.2 Hz), 1.63 (m, 4H), 2.83 (t, 4H, J = 7.5 Hz), 4.36 (q, 4H, J = 7.2 Hz), 10.28 (brs, 2H) ppm; C-13 nmr: 0.26, 14.1, 14.8, 23.8, 27.8, 60.5, 99.5, 101.5, 104.3, 119.1, 128.6, 136.1, 160.7 ppm. *Anal.* Calcd. for $C_{30}H_{44}N_2O_4Si_2$ (552.9): C, 65.18; H, 8.02; N, 5.07. Found: C, 65.15; H, 7.91; N, 4.72.

Diethyl 3,3′-bis(3-hydroxyprop-1-ynyl)-4,4′-di-*n*-propyl-2,2′-bipyrrole-5,5′-dicarboxylate (**1b**). Diiodopyrrole **10** (0.3 g. 0.7 mmoles), bis(triphenyl-phosphine)palladium(II) dichloride (0.05 g, 0.07 mmoles), cuprous iodide (0.03 g, 0.14 mmoles) and propargyl alcohol (0.16 g, 0.16 ml, 2.8 mmoles) were treated as above the syntheses of **1a**. The yield of (**1b**) was 0.17 g, 0.36 mmol (51%). It had mp 130-131°C; ir (KBr): 3450, 1675, 1454, 1278, 1140, 780 cm^{-1}; H nmr: 0.94 (t, 6H, J = 7.4 Hz), 1.35 (t, 6H, J = 7.1 Hz), 1.54 (m, 4H), 2.70 (t, 4H, J = 5.9 Hz), 3.01 (t, 4H, J = 7.4 Hz), 3.85 (t, 4H, J = 5.9 Hz), 4.32 (q, 4H, J = 7.1 Hz), 9.50 (brs, 2H), 13.5 (brs, 2H) ppm; C-13 nmr: 14.1, 14.5, 23.7, 30.4, 51.7, 60.9, 77.9, 93.5, 120.3, 120.6, 132.2, 135.12, 160.1 ppm. *Anal.* Calcd. for $C_{26}H_{32}N_2O_6$ (468.6): C, 66.65; H, 6.88; N, 5.98. Found: C, 66.43; H, 7.24; N, 6.11.

Diethyl 3,3′-Bis(4-hydroxybut-1-ynyl)-4,4′-di-propyl-2-2′-bipyrrole-5,5′dicarboxylate (**1c**). Diiodopyrrole **10** (0.3 g, 0.7 mmoles), bis(triphenyl-phosphine)palladium(II) dichloride (0.05 g, 0.07 mmoles), cuprous iodide (0.03 g, 0.14 mmoles) and 3-butyn-1-ol (0.2 g, 0.21 ml, 2.8 mmoles) were treated as above for **1a**. The yield of (**1c**) was 0.21 g, 0.43 mmol (62%). It had mp 139-140°C; ir (KBr): 3415, 3249, 2957, 2150, 1677, 1454, 1277, 1140, 793 cm^{-1}; H nmr: 0.94 (t, 6H, J = 7.4 Hz), 1.35 (t, 6H, J = 7.1 Hz), 1.54 (m, 4H, 2.70 (t, 4H, J = 7.1 Hz), 9.50 (brs, 2H) ppm; C-13 nmr: 14.0, 14.2, 24.2, 24.5, 27.5, 60.2, 60.8, 73.8, 94.4, 118.6, 119.9, 121.3, 134.6, 160.9 ppm. *Anal.* Calcd. for $C_{28}H_{36}N_2O_6$ (496.6): C, 67.72; H, 7.31; N, 5.64. Found: C, 67.74; H, 7.38; N, 5.69.

Diethyl 3,3′-Bis(phenyl-1-ethynyl)-4,4′-di-propyl-2-2′-bipyrrole-5,5′dicarboxylate (**1d**).Diiodopyrrole 10 (0.3 g, 0.7 mmoles), bis(tri-phenyl-phosphine)palladium(II) dichloride (0.05 g, 0.07 mmoles), cuprous iodide (0.03 g, 014 mmoles) and phenylacetylene (0.36 g, 0.38 ml, 3.5 mmoles) were dissolved in 15 ml freshly distilled triethylamine and treated as above for **1a**. The yield of (**1d**) was 0.15 g, 0.27 mmole (38%). It had mp 124-125°C; ir (KBr): 3246, 2249, 1705, 1675, 1456, 1263, 1105, 692 cm^{-1}; H nmr (d$_2$-dichloromethane): 0.95 (t, 6H, J = 7.4 Hz), 1.37 (t, 6H, J = 7.14 Hz), 1.57 (m, 4H), 3.05 (t, 4H, J = 7.4 Hz), 4.32 (q, 4H, J = 7.14 Hz), 7.39 (m, 6H), 7.54 (m, 4H), 9.44 (brs, 2H) ppm; C-13 nmr: 14.2, 14.6, 23.9, 27.8, 60.6, 83.5, 95.9, 104.3, 119.4, 123.3, 128.3, 128.6, 128.7, 131.7, 135.9, 160.7 ppm. *Anal.* Calcd. for $C_{36}H_{36}N_2O_4$ (560.7): C, 77.12; H, 6.47; N, 5.00. Found: C, 76.97; H, 6.47; N, 5.00.

Acknowledgments. We thank the National Institutes of Health (NICHD 17779) for generous support. E.N. was an R.C. Fuson Graduate Assistant.

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