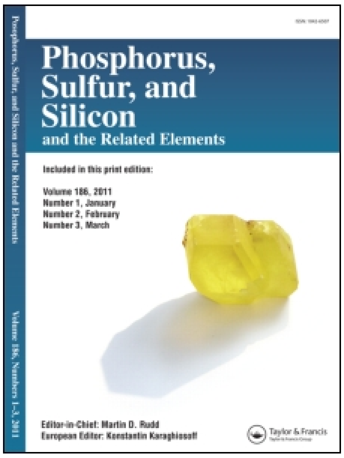

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Synthesis and Characterization of 2,5-Bis(2-pyridyl)thiophene

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SYNTHESIS AND CHARACTERIZATION OF 2,5-BIS(2-PYRIDYL)THIOPHENE

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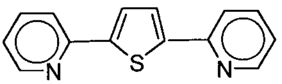
*2-[2-(Trimethylsilyl)ethynyl] pyridine (**6**) was prepared in 95% yield by reaction of 2-bromopyridine with trimethylsilylacetylene in triethylamine in the presence of bis(triphenylphosphine)Palladium(II) chloride and Copper(I) iodide. Desilylation of (**6**) by refluxing with sodium hydroxide in methanol (yield 95%) of 2-ethynylpyridine (**5**). Oxidative coupling of (**5**) in pyridine by oxygen in the presence of Copper(I) chloride gives 70% yield of 1,4-bis(2-pyridyl)1,3-butadiyne (**4**). Reaction of **4** with sodium sulfide affords 100% of 2,5-bis(2-pyridyl) thiophene (**1**).*

Keywords: 2,5-Bis(2-pyridyl)thiophene

2,2′:5′,2″-Terthiophene is a biologically active natural product, it was found in plants of family compositae. It shows nematicidal and fungicidal activity.[1–5] It was found that thiophene[6,7] and pyridine[8–11] are of interest as repeating units for the construction of electroconductive polymers, (**2**) and (**3**) respectively. Much of the research has been focused on modification of the base monomers and oligomers, specifically the alkyl derivatives which yield soluble polymers with improved conductivity. Oligopyridines and mixed oligopyridylthiophenes have resulted in a varity of new metal complexes. For example, α-sexipyridine[12] forms a double helical complexe with Cd^{+2}, 6-(2″-thienyl)-2,2′-bipyridine[13] exhibits a wide range of bond modes which



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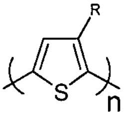

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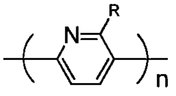

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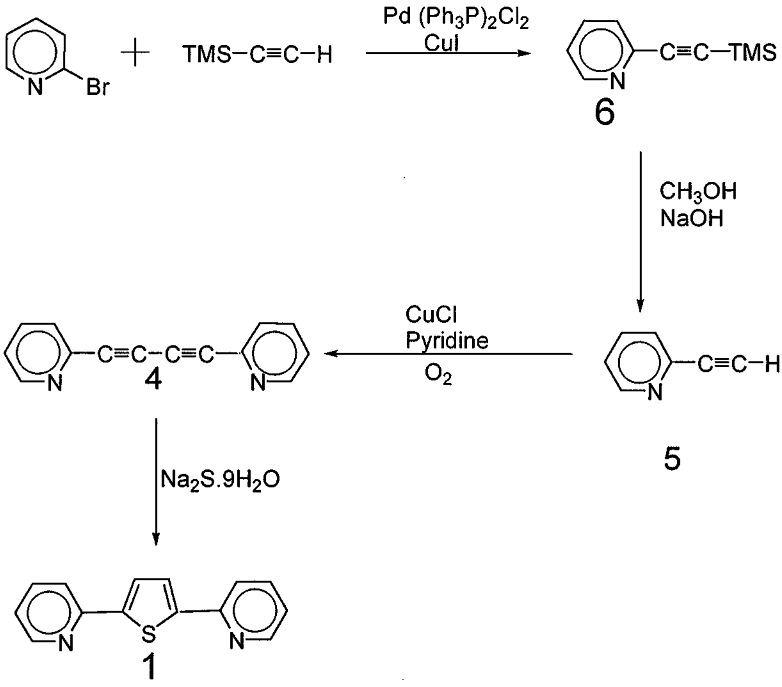
include bidentate N,N-donor, terdentate N,N,S-donor, and cyclometalated N,N,C-donor. Kumada[14] introduced a convenient synthesis for a varity of terheterocyclic compounds based on grignard compounds in the presence of nickel catalyst. However, thienopyridines and bipyridines were prepared in low yields. In view of the above, 2,5-bis(2-pyridyl)thiophene (**1**) was prepared via sulfide cyclization of 1,4-bis(pyridyl)-1,3-butadiyne. Herein, its synthesis and characterization is described.

SYNTHESIS

The synthesis of 2-ethynylpyridines has been described in the literature,[15] but the method is tedious and the overall yield is low. 2-Ethynylpyridine (**5**) was prepared in 90%. This involves the coupling of 2-bromopyridine with trimethylsilylacetylene[16] in the presence of bis(triphenylphosphine)Palladium(II)dichloride and copper(I) iodide in triethylamine followed with desilylation[17] with sodium hydroxide in methanol (Scheme 1).



SCHEME 1

2,6-Bis(pyridyl)thiophene (**1**) was prepared in quantitative yield via the interaction of sodium sulfide with 1,4-bis(2-pyridyl)-1,3-butadiyne (**4**), it is a good method for preparing oligomers with an odd number of thiophene rings. **4** was prepared in 70% yield from the oxidative coupling of 2-ethynylpyridine (**5**) in the presence of copper(I) chloride in pyridine shaken with oxygen bubbling (Scheme 1). Transition metal complexes of **1** is in progress. Structures of new compounds were based on elemental analysis data, ^{1}H-NMR, ^{13}C-NMR, and mass spectrometry.

EXPERIMENTAL

Melting points were determined on electrothermal melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on Brucker AM-300 spectrometer for solution in $CDCl_3$. The ^{1}H-NMR spectra were calibrated by using signals from the solvent referenced to $(Me)_4Si$. The elemental analysis were determined by M. H. W. laboratories (Phoenix, Arizona, U.S.A.). Mass spectra were determined by Finnigan MAT 731 spectrometer at 70 ev. Triethylamine and pyridine were dried over potassium hydroxide and were distilled before use. 2-Bromopyridine, dichloro[bis-(triphenylphosphine)] Palladium(II), $(Ph_3P)_2PdCl_2$ were purchased from Jansen Chemica. Trimethylsilylacetylene was prepared according to the literature.[16] $Na_2S.9H2O$ purchased from PSPARK Scientific Limited.

2-[2-(Trimethylsilyl)ethynyl]pyridine (6)[17]

Dichloro [bis(triphenylphosphine)]Palladium(II), 0.40 g and copper(I) iodide, 0.27 g were added to a solution of 5.0 g (0.032 mmol) of 2-bromopyridine and trimethylsilylacetylene 3.9 g (0.04 mmole) in dry triethylamine (50 ml) under nitrogen atmosphere. The reaction mixture was cooled in an ice bath for 1 h and allowed to stir at room temperature overnight. Water was added and the mixture was extracted with ether (4 × 50 ml), ether extract dried over anhydrous Na_2SO_4, filtered, and concentrated to a brown oil. This material was passed over a silica gel eluting with hexane, hexane was removed to afford colorless oil 5.32 g (95%) yield. This product was used in the next step without farther purification. ^{1}H-NMR ($CDCl_3$): δ, 0.22 (S, 9H), 7.15–7.60 (m, 3H), 8.53 (d, $J = 6.0$ Hz, 1H).

2-Ethynylpyridine (5)[15]

A solution of 5.0 g (0.028 mmole) of 2-[2-(Trimethylsilyl) ethynyl] Pyridine (**6**) in methanol (50 ml) and 1N sodium hydroxide solution

(30 ml) was stirred for 1 h at room temperature, acetic acid, 3.0 ml (0.028 mmole) was added. The mixture was concentrated using rotatory evaporator, the residue was extracted with ether (2 × 50 ml), ether washed with water and brine, dried over anhydrous Na_2SO_4, ether was removed to afford 2.5 g (90%) yield of brownish oil, vacuum distillation (73°C/12 mmHg) afford colorless oil. ^{1}H-NMR ($CDCl_3$): δ, 3.15 (S, 1H), 7.17–7.78 (m, 3H), 8.58 (d, J = 6.0 HZ, 1H).

1,4-Bis(2-pyridyl)-1,3-butadiyne (4)[18]

Copper(I) chloride, 0.29 g was added to a solution of 2-ethynylpyridine, 0.375 g (0.036 mmole) in dry pyridine (30 ml), and the mixture bubbled with oxygen gas for 1 h; the color of the solution turned black. The mixture was poured into water 300 ml, no precipitate was formed. The reaction mixture was extracted with chloroform (3 × 40 ml), the solution was dried over anhydrous calicum chloride, evaporation of solvent using rotatory evaporator afford black oily product, evaporation in fume hood overnight to remove residual pyridine afford black solid. Crystallization from CCl_4 using charcoal afford white shinny crystals, 2.4 g (70%), m.p. = 120°–121°C. ^{1}H-NMR ($CDCl_3$, 300 MHZ): δ, 7.27 (m, 1H), 7.52 (broad doublet, 1H), 7.67 (m, 1H), 8.60 (d, J = 5.0 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 73, 81, 124, 128, 136, 142, 150. Anal. Calcd. For $C_{14}H_8N_2$: C, 82.33, H, 3.95. Found: C, 81.55; H, 3.83. MS(EI) [m/e (intensity)]: 205 (22), M^+ 204 (100), 203 (26), 177 (11), 176 (11), 164 (2), 151 (12), 124 (4), 100 (4.5), 99 (8).

2,5-Bis(2-pyridyl)thiophene 1

A solution of 1,4-bis(2-pyridyl)-1,3-butadiyne 0.74 g (3.6 mmol) and sodium sulfide nonahydrate, $Na_2S.9H_2O$ in dry tetrahydrofuran (30 ml) was refluxed overnight. THF was removed and the residue was extracted with hexane (2 × 20 ml), hexane was removed to afford light golden crystals, 0.82 g (100%) yield m.p. 158–159°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.13 (m, 1H), 7.63 (S, 1H), 7.70 (m, 2H), 7.58 (d, J = 5.0 Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 119, 122, 126, 127.8, 136.4, 149. Anal. Calcd. for $C14H_{10}N_2S$: C, 70.56; H, 4.23. Found: C, 69.30; H, 4.20. MS (EI) [m/e (intensity)]: 204 (7), 139 (18), M^+ 238 (100), 237 (20), 205 (19), 160 (7), 78 (11).

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