Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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M. Wasgindt [a] & E. Klemm [a]
[a] Institut für Organische Chemie und Makromolekulare Chemie der Friedrich-Schiller Universitat Jena , Humboldtstr. 10, D-07743, Jena
Published online: 17 Sep 2007.

To cite this article: M. Wasgindt & E. Klemm (1999) Preparation of a Novel 1,4-Pyridylphenylene Derivative For Synthesis of New Rigid Backbone Conjugated Polymers, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 29:1, 103-110, DOI: 10.1080/00397919908085740

To link to this article: http://dx.doi.org/10.1080/00397919908085740

SYNTHETIC COMMUNICATIONS, 29(1), 103-110 (1999)

PREPARATION OF A NOVEL 1,4-PYRIDYLPHENYLENE DERIVATIVE FOR SYNTHESIS OF NEW RIGID BACKBONE CONJUGATED POLYMERS

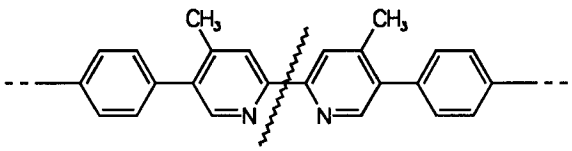
M. Wasgindt and E. Klemm*

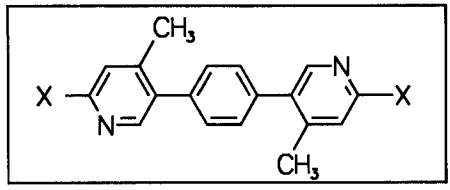
Institut für Organische Chemie und Makromolekulare Chemie der Friedrich-Schiller Universität Jena, Humboldtstr. 10, D-07743 Jena

ABSTRACT: High yield synthesis of 1,4-bis-(2-bromo-4-methyl-5-pyridyl)-benzene as monomer for conjugated polymers.

Since the first demonstration of organic polymer light emitting diodes, material research in this area has intensified[1]. Conjugated polymers with hight quantum yields of fluorescence are required for this application. Up to now, work has focussed primarily on the paraphenylene[2], paraphenylene vinylene[1] and thiophene[3] families of conjugated polymers. There has been little study of polyarenes with substituted pyridine and bipyridine units[4,5]. In this paper, we wish to present a simple monomer block for a polymer with exact repeating phenylene-bipyridine units.

* To whom correspondence should be addressed





1a: X=NH_2

1b: X=Br

figure 1: The desired polymerstructure and monomer block

The aspired polymerizations are based on the Suzuki-reaction[5], first established by Suzuki and Miller in the eighties[6,7]. Poly-p-phenylenes have been synthesized using this strategy with good results[8,9].

Our strategy for an efficient synthesis of **1b** is based on the diborolan **4**. The use of pinacol for esterfication is in near agreement to the desired goal; an excellent chloroform soluble derivative of a di-boronic acid, without any problems caused by the boronic acid structure (e.g. deboronations, forming of anhydrids, only slightly solubility in common organic solvents except dimethylsulfoxid) in Suzuki-reactions.

The unfunctionalized diborolan **4** was shown by T. Ishiyama[11] in the milligramme scale. Benzene-1,4-diboronic acid was first synthezised by Coutts et. al. in 1970 using a „Grignard"-pathway[12]. We decided an alternative way for synthesis of the unfunctionalized diborolan **4** in the gramme scale. p-Di-bromobenzene **2** is freshly sublimed; lithiation with butyllithium and interception of the intermediate p-di-lithiumbenzene with bis-dimethylamino-bromo-borane leads to another intermediate **3** which is also

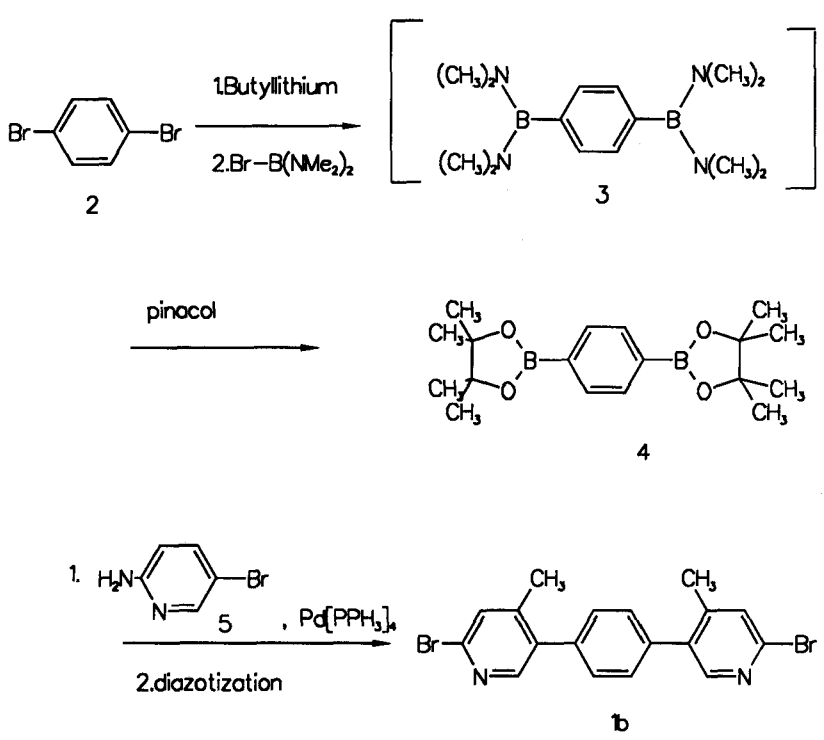


figure 2: Synthesis of the monomer

not fully characterized but isolated under argon atmosphere and mesured by ^{1}H-NMR and the mass spectrum.

After esterfication with pinacol, we get the diborolan **4** as white crystals in a real good quality ($C_{18}H_{28}B_2O_4$ (329.82): calc. C 65.55%, H 8.49%, found C 65.19%, H 9.00%). The unprotected 2-amino-5-bromo-4-picoline **5** reacts in a clean Suzuki-reaction (100%); the classical diazotization by Sandmeyer concludes the synthetic procedure with the monomer **1b**.

Experimental

The NMR spectra were recorded on a Bruker AC 250 and DRX 400 MHz spectrometer with $CDCl_3$, DMSO-d6 and acetic acid-d4 as the solvents. The

chemical shifts are referenced to TMS. The mass spectrum was obtained on a SSQ-710 (Finnigan Mat) spectrometer. The melting points were determined a Büchi 530 melting point apparatus. The CHN-analysis were done with a Leco CHNS-932 apparatus.

Bis-dimethylamino-bromoborane[13] is synthezised according to literature. 2-Amino-4-picoline is commercially available (FLUKA).

Procedure:

2-Amino-5-bromo-4-methylpyridine (5):

37g Bromine (0.23mol, 12cm^3) was added in 15min with shaking to a solution of 22g 2-amino-4-methylpyridine (0.2mol) in 100ml of 20% sulphuric acid. After allowing the mixture to react for another 15min, 250ml of a 20% aqueous sodium hydroxide solution were added, to get a deep-brown reaction mixture with a white voluminous precipitation. After thoroughly soxlett-extraction (15h) with diethylether the resultant clear-brown solution is washed with water and dried over anhydrous magnesiumsulfate. Finally, removing the solvent under reduced pressure, the rough-product is separated by chromatography (hexane/acetic acid ethylester 2:1); to do this, the top of the chromatography column is filled with the dry powder of the rough-product. You isolate m=14.5g (40%) of a yellow-crystalline powder with a melting point of m.p. 134°C. ^{1}H-NMR($CDCl_3$, 250MHz): δ= 2.24(s, 3H, $-CH_3$), 4.23(s, broad, 2H, $-NH_2$), 6.37(s, 1H, H^3), 8.05(s, 1H, H^6) ppm, ^{13}C-NMR($CDCl_3$, 250MHz): δ= 22.24, 110.30, 111.72, 148.04, 149.07, 157.56 ppm, mass spectrum: m/z= 188(M/98), 186(M/100), 162(30), 160(32), 159(34), 158(33), 107(14), 80(48), 53(34), 28(47), $C_6H_7BrN_2$(187.04): calc. C 38.53%, H 3.77%, N 14.97%, Br 42.72%, found C 38.65%, H 3.96%, N 15.07%, Br 42.23%.

Phenyl-1,4-diboronicacid-tetrakis-dimethylamid (3):

64ml of a 1.6M solution of n-butyllithium in hexane are dripping in a solution of 11.0g 1,4-dibromobenzene (47mmol) in 600ml dry petrol ether (boiling

range 30-60°C) within a period of 15min. The resulting light yellow clear solution is refluxed for 22h. Using a wide transfer needle, the resulting suspension phenylene-dilithium/LiBr/petrol ether is flushed over within 15min to a clear solution of 11.4g freshly distilled bis-dimethylamino-bromoborane (64mmol) in 100ml dry hexane at a temperature of -40°C. The dry ice/ethanol bath is put away and the reaction suspension has to be stirred for 12h at room temperature. A G4-fritte is piled with silica gel, and the white precipitate of the suspension is filtered off under inert gas atmosphere. In a high vacuum, the petrol ether/hexane is rapidly distilled from filtrate, which is continues turbid, so isolating a white-yellow powder with the exact melting point 72°C. The measured spectra indicate, that two molecules dimethylamine are coordinated to both boron centres. ^{1}H-NMR(250MHz, DMSO): δ= 2.22(s, broad, 36H, -CH_3), 3.35(s, broad, -NH), 7.06(s, 4H, aromatic-H) ppm, mass spectrum: m/z=275(M/14), 274(M/100), 273(M/92), 272(M/36), 230(50), 229(29), 214(17), 190(7), 171(13), 170(8), 147(21), 99(90), 98(50), 85(12), 83(13), 70(8), 56(17), 44(22).

Phenyl-1,4-diboronicacid-bis-pinacolester (4):

In an inert gas apparatus, a solution of 5.9g pinacol in 60ml dry benzene is added at low temperature (ice/salt bath) to a solution of 6.8g(19mmol) phenyl-1,4-diboronicacid-tetrakis-dimethylamid-bis-dimethylamino complex in 120ml dry hexane. 59ml of a 1.7M solution of dry HCl in diethylether is dropped in also, the resulting solution is stirred for 12h. After filtration of the white precipitate, the benzene filtrate is distilled under reduced pressure and the white powder is recrystallized from benzene, finally to isolate 1.3g(21%) white crystalls with the melting point 226°C.

^{1}H-NMR(250MHz, $CDCl_3$): δ= 1.33(s, 24H, -CH_3), 7.78(s, 4H, aromatic-H) ppm, ^{13}C-NMR(250MHz, $CDCl_3$): δ= 24.86, 83.83,

128.22, 133.87 ppm, mass spectrum: m/z= 331(M/9), 330(M/34), 329(M/19), 315(34), 314(19), 273(24), 272(13), 247(29), 244(100), 243(30), 231(88), 230(50), 215(19), 158(22), 144(36), 131(50), 83(30), 43(43), $C_{18}H_{28}B_2O_4$ (329.82):calc. C 65.55%, H 8.49%, found C 65.19%, H 9.00%.

1,4-bis-(2-amino-4-methyl-5-pyridyl)-benzene (1a):

In an inert gas apparatus, 2-amino-5-bromo-4-methylpyridine (1.5g, 8mmol), phenyl-1,4-diboronic acid-bis-pinacolester (1.3g, 4mmol), tetrakis-(triphenylphosphine)-palladium (0) (81mg, 0.07mmol) are suspended in a two-phase system toluene (oxygen-free, V=180ml)/2M sodium carbonate solution (oxygen-free, V=60ml). After waiting for a few minutes, you will get a clear two-phase solution, which is refluxed for 60h in an inert atmosphere. The white-brown precipitate is filtered off a G3-fritte. After drying in vacuum you isolate 1.1g(93%) of a white-brownish powder, which does not melt untill a temperature of 250°C. ^{1}H-NMR(250MHz, acetic acid-d4): δ= 2.30(s, 6H, -CH_3), 6.96(s, 2H, pyridine-aromatic-H^3), 7.49(s, 4H, phenyl-aromatic-H), 7.82(s, 2H, pyridine-aromatic-H^6) ppm, ^{13}C-NMR(250MHz, acetic acid-d4): δ= 114.23, 128.23, 130.71, 135.31, 136.15, 154.65, 155.93 ppm, mass spectrum: m/z= 292(M/20), 290(M/100), 145(19), 131(14), 117(10).

1,4-Bis-(2-bromo-4-methyl-5-pyridyl)-benzene (1b):

A solution of 2.9g 1,4-bis-(2-amino-4-methyl-5-pyridyl)-benzene (0.01mol) in 30ml acetic acid (100%) and 12ml of 48% HBr/water is cooled to -5°C. Bromine (2.4ml) is carefully dropped in within a period of 15min, looking forward, that the suspension can be stirred in a good way. The deep-red suspension is stirred for 20min at -5°C. Using a dropping

funnel, a solution of 3.5g sodium nitrite in 6ml water is added, when violent nitrogen generated. The suspension must be stirred for another hour at low temperature. After „neutralisation" with diluted sodium hydroxide solution reaching the basic range, the deep-brown precipitate is filtered off. You isolate 1.8g (43%) light-yellow needles (m.p.=196°C) after separation by flash chromatography using hexane/acetic acid ethylester 2:1 as the eluent. Fluorescence spectra (dioxane): absorption maximum 287nm, fluorescence band 385nm, ^{1}H-NMR(250MHz, $CDCl_3$): δ= 2.3(s, 6H, $-CH_3$), 7.37(s, 4H, phenyl-aromatic-H), 7.42(s, 2H, pyridine-aromatic-H^3), 8.21(s, 2H, pyridine-aromatic-H^6) ppm, ^{13}C-NMR(250MHz, $CDCl_3$): δ= 19.80, 129.03, 129.39, 136.42, 136.46, 141.17, 147.71, 149.92 ppm, mass spectrum: m/z= 422(M/7), 421(M/41), 420(M/28), 419(M/100), 418(M/33), 417(M/51), 416(M/11), 89(11), $C_{18}H_{14}Br_2N_2$ (418.01): calc. C 51.71%, H 3.35%, N 6.69%, found C 51.64%, H 3.78%, N 6.16%.

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Accepted April 25, 1998