Synthesis of a Linear Oligomeric Styrylpyrrole Using Multiple Heck and Wittig Reactions

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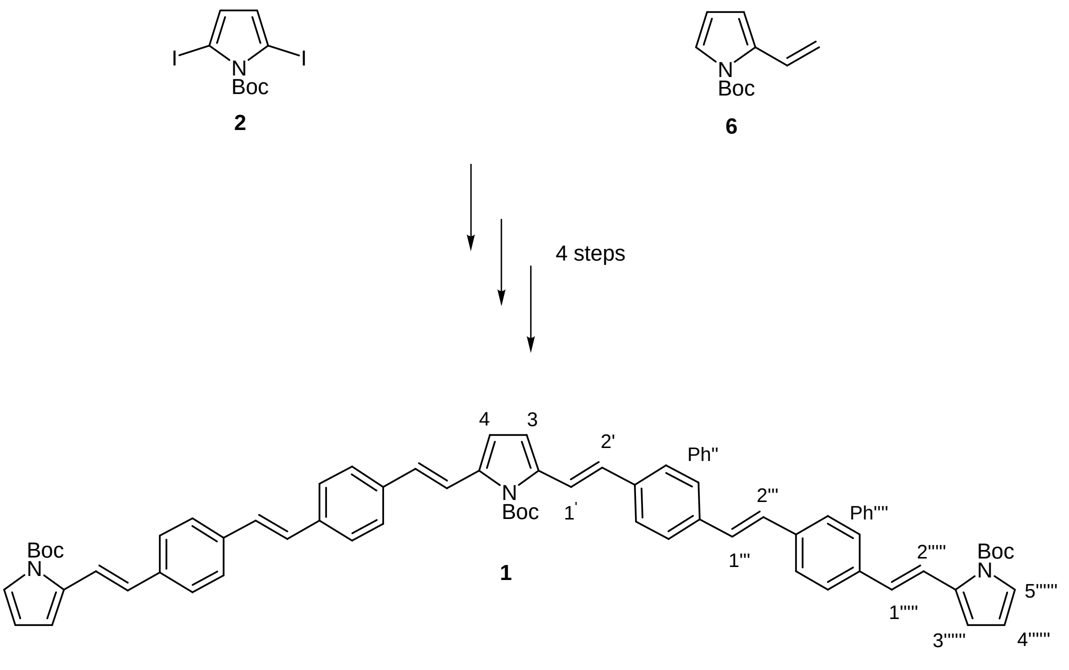
Abstract: The linear mixed oligomer **1** consisting of three pyrrole and four divinylbenzene moieties was synthesized by two twofold Heck and Wittig reactions in four steps starting from diiodopyrrole **2** and vinylpyrrole **6**.

Key words: Heck reaction, oligomers, organic conductors, palladium, polyenes, pyrroles

The preparation of well defined oligomers with a conjugated π-system has become an important field in organic chemistry over the past years.[1,2] This is mainly due to the unusual electronic properties of these compounds that make them suitable as organic conductors.[3] While there had been a substantial progress in the synthesis of many kinds of linear π-conjugated oligomers, monodisperse pyrrole containing systems remained difficult to obtain.[4] In the last years we have shown that the combination of several transition metal catalyzed reactions is a powerful tool for the efficient construction of complex molecules in very few steps.[5] It was therefore our intention to develop a synthetic route to a novel class of pyrrole containing π-conjugated oligomers using multi-fold palladium catalyzed transformations.

Here we describe the synthesis of the oligomeric π-system **1** which consists of three pyrrole and four divinylbenzene moieties (Scheme 1). This compound, to our knowledge, is the longest linear π-conjugated pyrrole containing oligomer[6] of defined structure and was obtained from the pyrroles **2** and **6** by a combination of twofold Heck[7] and Wittig reactions.

During our preliminary studies[8] we have observed that the *tert*-butoxycarbonyl moiety (Boc) as a *N*-protecting group[9] at the pyrrole units is most suitable in Pd-catalyzed reactions. All other protecting groups that we examined in this context, as for example the *p*-toluenesulfonyl or the ethoxycarbonyl group led to poorer results or were not applicable at all. On the other hand, unprotected pyrroles were not appropriate due to their low stability[10] and in addition, they expressed a decreased regioselectivity in Heck reactions. Thus, we have shown that the Pd-catalyzed reaction of iodopyrroles containing electron donating groups such as methyl groups in the 3- or 4- position with styrenes give mixtures of linear and branched prod-



Scheme 1

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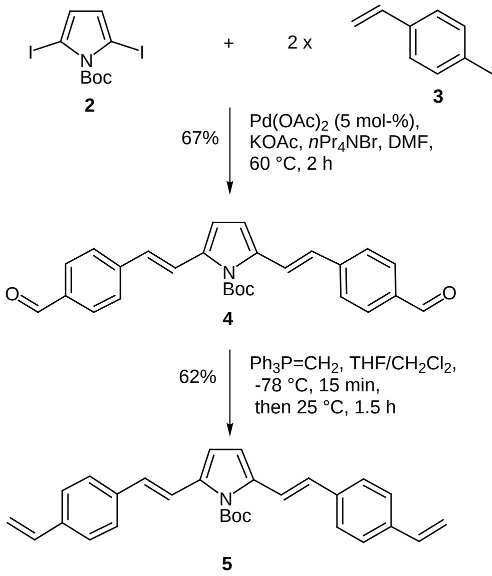
ucts. This is in accord with the findings of Hallberg et al. who observed that for electron rich styrenes α-arylation is favored.[11] However, in the reaction of the pyrroles steric reasons may also be of some importance. A practical advantage of the *tert*-butoxycarbonyl protecting group is the fact that it diminishes π-stacking effects and therefore increases the solubility of the products. As a starting material for the synthesis of **1** we employed the diiodopyrrole derivative **2**[12] (Scheme 2).

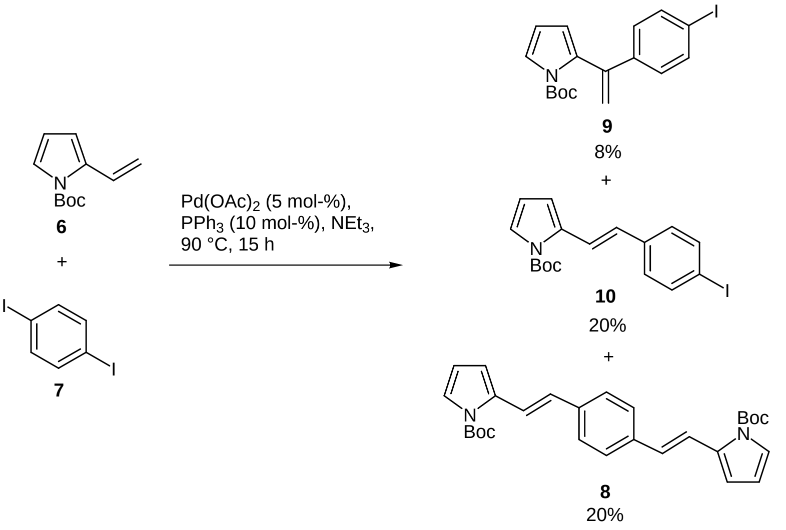


Scheme 2

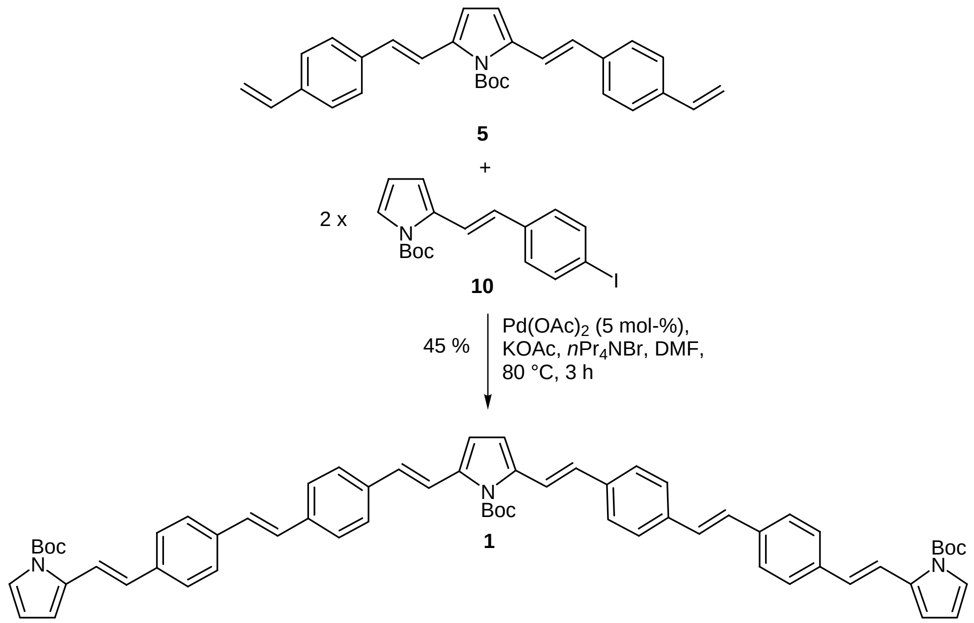
The twofold Heck reaction of **2** with two equivalents of *p*-vinylbenzaldehyde **3**[13] in the presence of 5 mol% palladium acetate, 4 molar equivalents of potassium acetate and 1 molar equivalent of tetrapropylammonium bromide in dimethylformamide for 2 hours at 60 °C gave **4** in 67% yield. The reaction is completely regioselective; thus, the attack occurred exclusively at the less substituted position of the vinyl group in **3**. A twofold Wittig reaction of **4** with $Ph_3P=CH_2$ then furnished the divinyl compound **5** in 62% yield. The final step in the synthesis of **1** was the coupling of **5** with two equivalents of the styrylpyrrole **10** again using a twofold Heck reaction. Reacting **6**[14] with 1.5 equivalents of 1,4-diiodobenzene **7**[15] in the presence of 5 mol% palladium acetate and 10 mol% triphenylphosphane in triethylamine for 15 h at 90 °C gave **10** in a yield of 20%, together with 20% of the styryldipyrrole **8** and 8% of the branched α-arylated coupling product **9** (Scheme 3).

The low yield of **10** is partly caused by difficulties in the chromatographic separation due to similar R_f-values of **9** and **10**. Astoundingly, the use of a tenfold excess of **7** in the reaction with **6** had only a marginal influence on the product ratio. In the presence of a silver salt the yield even decreased. Instead, it may be possible to prepare **10** in a more selective way using a multi-step approach. Another promising way would be the application of 4-iodobenzenetriflate in the presence of a catalyst described by Fu.[16] The twofold Heck reaction of **5** and **10** in the presence of 5 mol% palladium acetate, 4 molar equivalents of potassium acetate and 1 molar equivalent of tetrapropylammonium bromide in dimethylformamide for 3 hours at 80 °C furnished nearly pure **1**[17] regioselectively in over 70% yield. Chromatographic purification of crude **1** led to a dark red poorly soluble solid with an absorption maximum at $\lambda_{max} = 436.0$ nm (lg $\varepsilon = 4.809$) in 45% yield based on **5** (Scheme 4).[18] The best solvent for **1** is warm chloroform.

The ^{1}H NMR spectrum of **1** is quite simple due to the symmetry of the molecule. It shows four different signals for the pyrrole hydrogens. Those of the two external pyrrole moieties resonate as a triplet at $\delta = 6.20$ ppm and two multiplets at $\delta = 6.58$ ppm and $\delta = 7.29$ ppm which are characteristic for 2-substituted pyrroles. The two hydrogens of the central pyrrole unit resonate as a singlet at $\delta = 6.59$ ppm. The olefinic hydrogens are divided into three groups; the signals for the hydrogens at the four double bonds connected to a pyrrole moiety are found at $\delta = 6.88$



Scheme 3



Scheme 4

ppm and δ = 7.56 ppm (2’-H and 1’-H) as well as at δ = 6.89 ppm and δ = 7.79 ppm (1’’’’’-H and 2’’’’’-H) with J = 16.5 Hz in all cases. The hydrogens of the two stilbene subunits resonate as a singlet at δ = 7.10 ppm. The signals of the aromatic hydrogens are found as a multiplet at δ = 7.39-7.55 ppm and those of the carbamate moieties as two singlets at δ = 1.64 ppm and δ = 1.68 ppm. The *E*-configuration of the double bonds at the pyrroles can clearly be supposed from the large coupling constants of J = 16.5 Hz. The *E*-configuration of the stilbene subunits can not be deduced directly from the ^{1}H NMR spectrum; however the *Z*-compound should be much less stable und should isomerize to the *E*-compound, and on the other hand, the signals of the aromatic hydrogens should be more diversified due to shielding effects.

In conclusion, we have shown that defined oligomers of type **1** can be obtained in a straightforward modular approach by combination of several multiple Heck and Wittig reactions.

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(17) **1**: $R_f = 0.13$ (light petroleum ether/ EtOAc 10:1). IR (KBr): ν = 3022 cm^{-1}, 2976, 2928, 2854 (CH_2), 1740 (carbamate-C=O). UV ($CHCl_3$): λ_{max} (lg ε) = 245.0 nm (4.412), 436.0 (4.809). ^1H NMR (300 MHz/$CDCl_3$): δ = 1.64 (s, 18 H, $C(CH_3)_3$), 1.68 (s, 9 H, $C(CH_3)_3$), 6.20 (t, *J* = 3.6 Hz, 2 H, 4’’’’’’-H), 6.58 (m_c, 2 H, 3’’’’’’-H), 6.59 (s, 2 H, 3-H, 4-H), 6.88 (d, *J* = 16.5 Hz, 2 H, 2’-H)*, 6.89 (d, *J* = 16.5 Hz, 2 H, 1’’’’’-H)*, 7.10 (s, 4 H, 1’’’-H, 2’’’-H), 7.29 (dd, *J* = 1.6 Hz, 2 H, 5’’’’’’-H), 7.39-7.55 (m, 16 H, Ph-H), 7.56 (d, *J* = 16.5 Hz, 2 H, 1’-H)*, 7.79 (d, *J* = 16.5 Hz, 2 H, 2’’’’’-H)*. MS (FAB): $[M+1]^+$ 958.

(18) Compound **1** was prepared in an amount of 20 mg.

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