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Metal-Free Oxidative Cross-Coupling Reaction of Thiophene Iodonium Salts with Pyrroles

Koji Morimoto,[a] Akira Nakamura,[b] Toshifumi Dohi[a] and Yasuyuki Kita*[a],[b]

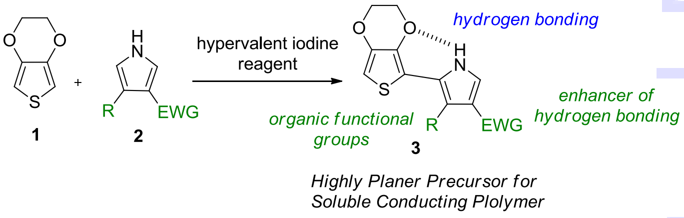
Abstract: The hypervalent iodine mediated oxidative metal-free cross-coupling reaction of thiophenes with various pyrroles has been developed. The corresponding thiophenes-pyrrole derivatives were obtained in moderate to high yields (up to 85%). This method features a high efficiency and regioselectivity, and functional-group tolerance. We further determined the highly planar characteristics of the EDOT-pyrrole biaryls caused by the intramolecular hydrogen bonding.

Introduction

The biaryl moiety as a key structures was found in many natural products, bioactive molecules, and functional materials due to their unique physical properties.[1] Therefore, the development of new and efficient cross-coupling reaction to prepare biaryls has attracted a great deal of attention.[2] Among them, a large number of straightforward methods that involve the oxidative coupling processes of two molecules of unfunctionalized aromatic compounds has been reported using oxidizing agents to produce these important biaryl compounds.[3] Recently, we reported the oxidative biaryl coupling reaction of aromatic compounds[4] and the coupling reaction of electron-rich heteroaromatic compounds[5,6] using hypervalent iodine(III) reagents. However, the efficient oxidative thienyl-pyrrole synthesis has not yet been achieved. This is because the control of the coupling products to avoid any unwanted oligomerization is particularly difficult due to their particularly lower oxidation potentials.[7]

The conventional approach for the thienyl-pyrrole synthesis of both the thiophene and pyrrole units involves the use of 1,4-dicarbonyl compounds.[8,9] In the case of the thiophenes, the 1,4-dicarbonyl compounds are reacted with sulfur sources.[10] By similar reactions, the pyrroles have been prepared *via* the condensation of 1,4-dicarbonyl compounds with nitrogen sources, *i.e.,* a reaction known as the Paal–Knorr synthesis.[8] These methods, although widely employed, are generally limited to the *2,5- di- or poly*-substituted thienyl-pyrroles at the thiophene and pyrrole rings. On the other hand, modern synthetic methods of the thienyl-pyrrole often rely on the versatile use of the Pd-catalyzed coupling reaction.[11] Thus, thienyl-pyrroles have been prepared by the Stille or Suzuki coupling of *N*-protected pyrrole stanannes or *N*-protected pyrrole boronic acid with thienyl-halogens. However, these strategies also have a limitation due to the substrates, since both the pyrrole-based metals and halides are unstable and reliant on the proper selection of the nitrogen-protecting group. Recently, the Pd-catalyzed direct arylation of heteroaromatics using aryl halides as coupling partners has been shown to be a very powerful method for the synthesis of arylated heterocycles.[12] Although these methods are more attractive than the other Pd-catalyzed cross-coupling reactions as they avoid the preparation of an organometallic derivative, the thienyl-pyrrole synthesis including the C-H activation method has scarcely reported.[13]

We now disclose the efficient oxidative synthesis of thiophene-pyrroles by using an appropriate choice of hypervalent iodine reagent. In addition, we have extensively characterized the high planarity of a new EDOT-pyrrole dimer determined by an X-ray structural analysis (Scheme 1).



Scheme 1. The oxidative metal-free synthesis of functionalized EDOT-pyrroles of high planarity by an enhanced intramolecular hydrogen bonding (EWG = electron-withdrawing group).

Results and Discussion

Recently, thienyl-pyrroles and their derivatives have received much attention as useful precursors for modifying the properties of corresponding polymers,[10] due to the ease of introducing substituents at the nitrogen atom into the pyrrole ring. On the other hand, the more successfully conducting polymers are poly(3,4-ethylenedioxythiophene) (PEDOT)[14,15] and polypyrrole.[16] The PEDOT shows a rigid coplanar backbone stabilized by the intramolecular S---O interactions.[17] Therefore, we consider that the possible intramolecular O--H--N hydrogen bond interaction of the EDOT-pyrrole might lead to finding a novel precursor of the oligomer and polymer. The development of a convenient synthesis of EDOT-pyrrole is important in organic chemistry, as these mixed dimers are expected precursors for synthesing regioregular conducting polymer.[18] Thus, we initially examined the coupling reaction of EDOT **1** using the commercially available pyrrole **2a** as a model

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[a] Dr. K. Morimoto, Dr. T. Dohi and Prof. Dr. Y. Kita
Ritsumeikan University
College of Pharmaceutical Sciences
1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan
Fax:(+81)-77-561-5829
E-mail: kita@ph.ritsumei.ac.jp

[b] Dr. A. Nakamura, Prof. Dr. Y. Kita
Ritsumeikan University
Research Organization of Science and Technology,
1-1-1 Nojihigashi, Kusatsu, Shiga, 525-8577,Japan
Tel. +81-77-561-5829; Fax. +81-77-561-5829

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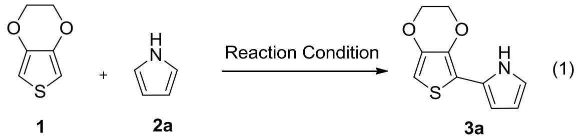
substrate under several conditions (Table 1, Eq. 1). The reaction didn't proceed using the common inorganic oxidants such as Fe(III) chloride or Mo(V) chloride.[19] We found that the coupling reaction took place when 2 equivalents of TMSBr and 1 equivalent of PhI(OH)OTs as the oxidant in $(CF_3)_2CHOH$ (HFIP) were used. The coupling product was produced in 51% yield.[4a] The yield was improved to 65% yield using phenyliodine bis(trifluoroacetate) (PIFA) as the oxidant (entry 4). We evaluated other iodine(III) reagents, but the use of PIFA provided superior results to the use of other iodine reagents, such as phenyliodine diacetate (PIDA) (entry 5). An another fluoroalcohol as TFE was less effective than HFIP (entry 6). The strongly Lewis acidic triflate or TMSI gave poor results (entries 7 and 8). Other ordinary organic solvents, such as CH_3CN and dichloromethane gave no coupling product. The advantages of the present method include the use of readily accessible starting materials, complete regiochemical control over the substituent placement, and metal-free methodologies. We also confirmed that the reaction did not proceed under other oxidative conditions which were recently reported using metal catalysts, *i.e.*, Pd salts with stoichiometric inorganic oxidants, such as $Cu(OAc)_2$ or AgOAc.[20]

Table 1. Optimization of reaction conditions[a)]

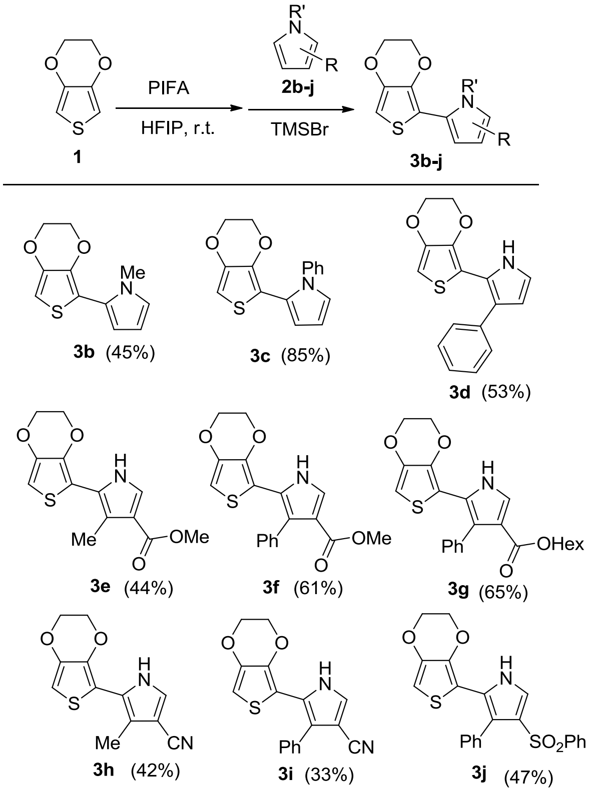


Entry	Reaction Condition	Time	Yield[b)] (%)
1	$FeCl_3$ $(CF_3)_2CHOH$ (HFIP)	24 h	n.d.
2	$MoCl_5$ HFIP	24 h	n.d.
3	PhI(OH)OTs, TMSBr HFIP	3 h	51
4	PIFA, TMSBr HFIP	//	65
5	PIDA, TMSBr HFIP	//	41
6	PIFA, TMSBr TFE	3 h	13
7	PIFA, TMSOTf HFIP	24 h	n.d.
8	PIFA, TMSI HFIP	24 h	trace

[a] Reaction conditions: EDOT **1** (0.4 mmol), pyrrole **2a** (1.2 mmol), TMSBr (0.8 mmol), and iodine reagent (0.4 mmol) in solvent (4 mL) at room temperature. [b] Yields are those for the isolated coupling product.

Encouraged by the results, the syntheses of different substituted thienyl-pyrroles were performed as shown in Table 2. Not only the *N-H* pyrrole **2a**, but also the *N*-methylpyrrole **2b** and *N*-phenylpyrrole **2c** were readily coupled with EDOT **1** in good yields. In the case of the 3-phenyl pyrrole **2d**, the coupling product **3d** was obtained as a single regioisomer. The synthesis of low band gap (*Eg*) materials having broad absorption bands represents one of the most efficient strategies to develop organic solar cells with higher efficiencies.[21] Therefore, we directed our attention toward the synthesis of α,α′–thienyl-pyrroles having electron-donating group (EDG) and electron-withdrawing group (EWG) as the substituents. These approaches to electronic heteroaromatic materials are desireable for reducing the band gap of polymers which is influenced by the HOMO and the acceptor LUMO energies.[22,23] Therefore, we challenged the coupling reaction of EDOT with pyrroles having EWG. As a result, pyrroles **2e** and **2f** having an electron-withdrawing group gave the desired coupling products **3e** and **3f** in good yields, respectively. The higher alkyl substituent **2g** did not affect the yield of the product **3g.** The cyano and sulfonyl substituted pyrroles **2i** and **2j** gave the coupling products **3i** and **3j** in moderate yields, respectively.

Table 2. Scope of substrates.[a, b)]



[a] Performed using EDOT **1** (1 equiv), PIFA (1 equiv), TMSBr (2 equiv) in HFIP at room temperature. [b] Pyrrole **2** (1.5 equiv) and TMSBr (2 equiv) was added after EDOT **1** reacted with PIFA in HFIP.

The crystallographic structure of a single crystal of EDOT-pyrrole **3f** has been analyzed by X-ray diffraction (Figure 1).[24] Interestingly, the structure of the molecule is perfectly planar with the thiophene and pyrrole rings in an *anti*-conformation as a result of the strong hydrogen bonding between the EDOT oxygen and pyrrole *NH* group. Thus, the N5---O3 distance of 2.764 Å is considerably shorter than the sum of the van der Waals radii of nitrogen and oxygen (3.07 Å). This result means that the intramolecular O---N hydrogen bond interaction by the aid of the electron-withdrawing ester group on the pyrrole ring leads to the self-planarization and rigidification of the π-conjugated system.[16] The observed downfield shift of the N-H hydrogen peak of ^{1}H-NMR spectroscopy clearly suggest the strong hydrogen bond even in organic solvent.

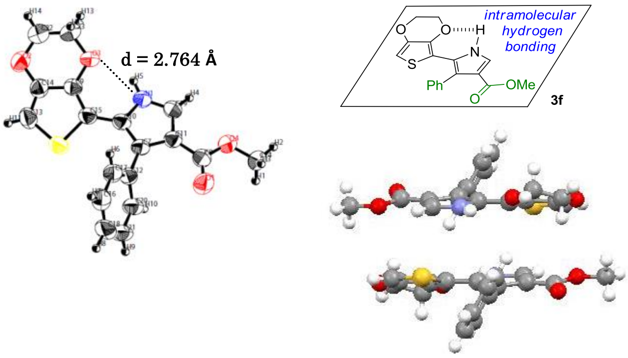


Figure 1. X-ray structure of highly planer dimer **3f**

Conclusions

In summary, the EDOT-pyrroles **3** were effectively synthesized by the oxidative coupling reaction using an appropriate hypervalent iodine reagent. Since this coupling method is quite simple and practical, it is compatible with the synthesis of a wide variety of related derivatives. Spectroscopic studies and thermal characterization revealed that the structure of the heteroaromatic moiety significantly influences these properties. Utilizing the high planarity of the EDOT-pyrrole, the oligomer and polymer of the EDOT-pyrrole would provide novel physical properties. The electronic properties of the oligomers based on these new building blocks are under investigation and will be reported in future publications.

Experimental Section

General Procedure for the Oxidative Coupling Reaction of EDOT with Pyrroles.

To a stirred solution of EDOT **1** (1 equiv) in HFIP (0.2 M), PIFA (1 equiv) was added at room temperature. After stirring for 3 hours, pyrrole **2a** and TMSBr (2 equiv) were sequentially added to the reaction mixture with stirring and then stirred for an additional 3 h under the same conditions, while the reaction progress was checked by TLC. Saturated aqueous sodium hydrogen carbonate was added to the mixture when the reaction completed. The aqueous phase was extracted with CH_2Cl_2. The extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (eluent: *n*-hexane/ CH_2Cl_2) to give the pure EDOT-pyrrole dimer **3a** (65% yield)

2-(2,3-Dihydrothieno[3,4-b]-1,4-dioxin-5-yl)-1*H*-pyrrole (3a)

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (1H, brs), 6.77-6.78 (1H, m), 6.29-6.30 (1H, m), 6.19-6.21 (1H, m), 6.10 (1H, s), 4.28-4.31 (2H, m), 4.21-4.23 (2H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 135.4, 125.5, 117.5, 111.1, 109.0, 104.6, 94.9, 65.0, 64.6 ppm; IR (KBr): 3427, 3109, 2980, 2929, 2872, 1693, 1551, 1497, 1445, 1366, 1175, 1070, 910, 795, 719, 654 cm^{-1}; HRFABMS: calcd for $C_{10}H_9NO_2S$ $[M]^+$ 207.0354, found 207.0357.

Methyl 5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-4-phenyl-1*H*-pyrrole-3-carboxylate (3f)

Yellow solid; mp 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (1H, brs), 7.46 (1H, d, *J* = 3.2 Hz), 7.32-7.41 (5H, m), 5.99 (1H, s), 4.31-4.33 (2H, m), 4.19-4.21 (2H, m), 3.62 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 140.8, 136.8, 134.3, 131.1, 128.0, 127.5, 124.2, 123.1, 121.9, 115.3, 109.3, 97.5, 65.2, 64.4, 50.8 ppm; IR (KBr): 3416, 2991, 2945, 2872, 1712, 1520, 1442, 1070, 750 cm^{-1}; HRFABMS calcd for $C_{18}H_{15}NO_4S$ $[M]^+$ 341.0722, found 341.0712.

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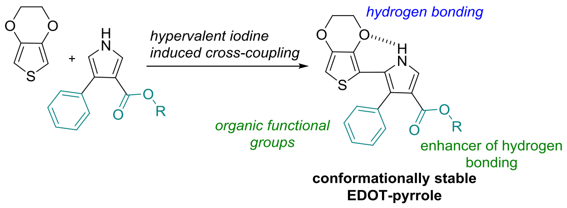
[24] CCDC 1035911 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif. For more detailed crystallographic data, see the CIF.

Layout 2:

COMMUNICATION



The efficient hypervalent iodine induced oxidative cross-coupling reamaction of 3,4-ethylenedioxythiophene (EDOT) with various pyrroles has been succeeded by optimization of the reagent. The corresponding EDOT-pyrrole derivatives were obtained in moderate to high yields (up to 85%). This method features a high efficiency and regioselectivity, and functional-group tolerance.

*one or two words that highlight the emphasis of the paper or the field of the study

Biaryl*

Koji Morimoto, [a] *Akira Nakamura,* [b] *Toshifumi Dohi,*[a] *and Yasuyuki Kita**[a], [b]

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Metal-Free Oxidative Cross-Coupling Reaction of Thiophene Iodonium Salts with Pyrroles