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An efficient synthesis of 5,5′-diaryl-2,2′-bichalcophenes

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Abstract—A convenient and high yielding synthesis of 5,5′-diaryl-2,2′-bichalcophenes (furans, thiophenes, and selenophenes) by the hexabutylditin-mediated homocoupling of 5-bromochalcophenes is described. This approach has been applied to the synthesis of the blue-light-emitting compound 5,5′-bis(4-aminophenyl)-2,2′-bifuryl (PFDA).

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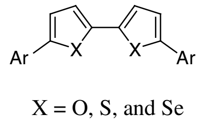
1. Introduction

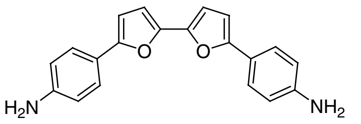
Bi- and oligo-chalcophenes (furans, thiophenes, selenophenes, etc.) continue to receive significant attention as advanced materials.[1] For example, 5,5′-diaryl-2,2′-bichalcophenes (**I**) have been studied as a result of their luminescent,[2] electrochemical,[3] and semiconducting[4] properties. Oligochalcophenes, particularly oligothiophenes,[5] have been heavily investigated as organic semiconductors, with particular application to thin-film transistors (TFTs),[1a,c] light-emitting devices (LEDs),[1b] and photovoltaics.[1d] This includes the unique oligoselenophenes, which have recently been investigated as a TFT material.[1e]

The preparation of 2,2′-bichalcophenes has historically involved classical heterocyclic ring-forming methods, such as the Trofimov and Paal–Knorr syntheses.[6] More recent approaches to 2,2′-bichalcophenes that do not involve ring formation include the sequential cross-coupling of metalated chalcophenes with aryl halides,[2,3,7] the Suzuki coupling of bromochalcophenes with arylboronic acids,[4d,7a,8] and the Heck arylation.[4c] Copper[9] or iron[10] mediated homocoupling of lithiated (or transmetalated) chalcophenes has also been heavily utilized; however, the presence of base sensitive functional groups (e.g., cyano) can limit this approach. The direct oxidative homocoupling of neutral chalcophenes at an unsubstituted site using a Pd/Ag combination[11] has also been described. Finally, a low yielding benzidine rearrangement has been employed to prepare 5,5′-bis(4-aminophenyl)-2,2′-bifuryl (PFDA, **II**), a blue-light-emitting compound utilized in the development of photoluminescent polyimides.[12]



X = O, S, and Se
Ar = aryl and heteroaryl

I



PFDA

II

The homocoupling of halogenated aryls by reaction with a hexaalkylditin and a palladium catalyst has been known for some time now.[13] Surprisingly, this reaction has received little attention thus far in the synthesis of bi- and oligochalcophenes,[14] although it represents a straightforward approach that should tolerate a variety of functional groups as anion formation is not required. As a result of our synthetic efforts to prepare biologically active[15] and fluorescent[16] diamidines, we have previously developed a convenient method for the preparation of 2-bromo-5-(4-cyanophenyl)chalcophenes.[17] We thus decided to explore the viability of the hexaalkylditin-mediated homocoupling of these brominated precursors for the direct synthesis of our targeted 5,5′-diaryl-2,2′-bichalcophenes (**I**). Herein, we describe our excellent results with this homocoupling approach. We also describe a new, higher yielding synthesis of PFDA (**II**) that employs this homocoupling reaction as a key step.

Keywords: Bichalcophene; Bifuran; Bithiophene; Biselenophene; PFDA; Homocoupling.

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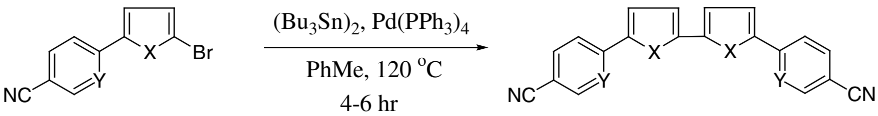

Scheme 1.

2. Results

As shown in Scheme 1, our conditions for homocoupling involved reaction of the 2-bromo-5-(4-cyanophenyl)chalcophenes (1 equiv) with hexabutylditin (0.6 equiv) in the presence of catalytic $Pd(PPh_3)_4$ (∼1.5–2 mol %) using refluxing toluene as solvent. After a period of 4–6 h, the insoluble product was filtered off and recrystallized from DMF to give the bifurans, bithiophenes, as well as biselenophenes in good to excellent yield (78–92%).[18] In addition to the phenyl-substituted bichalcophenes (Table 1, entries 1–3), the 2-pyridyl analogues were also obtained in similar high yield (entries 4–6). It is noteworthy that a good yield (77%) of the phenyl-substituted bifuran (entry 1) was obtained in an experiment employing excess (1.1 equiv) hexabutylditin, suggesting that the homocoupling product is preferred over the stannylated monochalcophene product. The opposite appears to be the case with certain benzene[19] and pyridine[20] derivatives.

To further illustrate the use of this homocoupling approach to bichalcophenes, the fluorescent bifuran PFDA (**II**)[12] was also prepared by this route. As shown in Scheme 2, bifuran **II** was readily obtained in 50% overall yield[21] from 2-bromo-5-(4-nitrophenyl)furan after homocoupling and nitro reduction by catalytic hydrogenation. The previously described route to **II** involves isolation of a diazonium and a 20% yielding benzidine rearrangement.[12d]

In conclusion, we have described a straightforward and high-yielding homocoupling approach to 5,5′-diaryl-2,2′-bichalcophenes. Considering the widespread and continued development of bi- and oligochalcophenes as advanced materials, including cyano-substituted derivatives,[22] it is expected that this approach will be of immediate interest to those synthesizing these type compounds.

Table 1.

Entry	X	Y	Yield[a]	Mp (°C)
1	O	CH	78	298–299
2	S	CH	91	298–300
3	Se	CH	92	285–286.5
4	O	N	81	>300
5	S	N	85	>300
6	Se	N	85	>300

[a] Yield of isolated, analytically pure compound.

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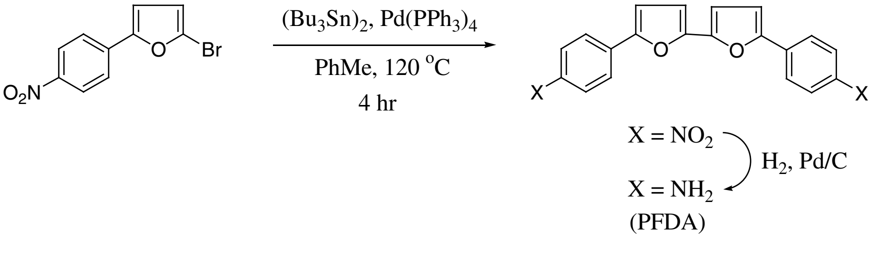

Scheme 2.

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18. Representative procedure: 5,5′-Bis(4-cyanophenyl)-2,2′-bithiophene (Table 1, entry 2). To a solution of 2-bromo-5-(4-cyanophenyl)thiophene (2.64 g, 10 mmol), and $Pd(PPh_3)_4$ (200 mg, 0.17 mmol) in toluene (40 mL) was added hexa-*n*-butylditin (3.48 g, 6 mmol). The reaction mixture was heated under N_2 at 120 °C for 6 h, then cooled, and the precipitate was filtered and washed with ether. Recrystallization from DMF gave a yellow crystalline solid (1.67 g, 91%), mp 298–300 °C. ^1H NMR (DMSO-d_6); δ 7.45 (d, $J = 4.2$ Hz, 2H), 7.68 (d, $J = 4.2$ Hz, 2H), 7.85–7.89 (m, 8H). ^{13}C NMR; δ 140.3, 137.1, 137.0, 132.5, 126.8, 125.7, 125.4, 118.0, 109.6. MS (*m*/*z*, rel int.); 368 (M^+, 100), 334 (5), 222 (8), 184 (20). High resolution MS calcd for $C_{22}H_{12}N_2S_2$: 368.04419. Observed 368.04476. Analysis for $C_{22}H_{12}N_2S_2$: Calcd: C, 71.71; H, 3.28. Found C, 71.48; H, 3.40.
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21. Heating 2-bromo-5-(4-nitrophenyl)furan (1.07 g, 4.0 mmol), hexa-*n*-butylditin (1.22 g, 2.1 mmol), and $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol, 1.25 mol %) for 4 h according to the representative procedure gave 5,5′-bis-(4-nitrophenyl)-2,2′-bifuran as a red solid (0.68 g, 90%), mp 280–283 °C. Recrystallization from DMF/MeOH gave the analytical sample with the same mp. ^1H NMR (DMSO-d_6): 7.18 (d, $J = 3.6$, 2H), 7.53 (d, $J = 3.9$ Hz, 2H), 8.05 (d, $J = 9.0$ Hz, 4H), 8.31 (d, $J = 9.3$ Hz, 4H). Analysis for $C_{20}H_{12}N_2O_6$: Calcd: C, 63.83; H, 3.21; N, 7.44. Found: C, 63.49; H, 3.37; N, 7.50. A suspension of the bis-nitro compound (0.75 g, 2.0 mmol) in EtOAc (100 ml) and EtOH (10 ml) was hydrogenated with 10% Pd/C (0.25 g, Lancaster) at 60 psi until uptake subsided (3 days). The mixture was then filtered over Celite and concentrated in vacuo to a brown solid (0.55 g). Recrystallization from benzene gave 5,5′-bis-(4-aminophenyl)-2,2′-bifuryl (PFDA, **II**) as a yellow/tan crystalline solid (0.35 g, 56%), mp 218–221 °C. A second recrystallization from EtOH gave fine golden scales, mp 221–222 °C (Lit.[12d] mp 203–205 °C). ^1H NMR (DMSO-d_6): 5.35 (br s, $2NH_2$), 6.61 (d, $J = 8.7$ Hz, 4H), 6.66 (d, $J = 3.6$ Hz, 2H), 6.70 (d, $J = 3.6$ Hz, 2H), 7.42 (d, $J = 8.7$ Hz, 4H). ^{13}C NMR (DMSO-d_6): 103.9, 107.1, 114.0, 118.1, 124.9, 143.9, 148.7, 153.8. MS (ES): *m*/*z* 317 (100%, MH^+). Analysis for $C_{20}H_{16}N_2O_2$: Calcd: C, 75.92; H, 5.10; N, 8.86. Found: C, 75.95; H, 5.05; N, 8.77.
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