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Palladium-Catalyzed C2 or C5 Direct Arylation of 3-Formylthiophene Derivatives with Aryl Bromides

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The system $Pd(OAc)_2$/dppb was found to be an efficient catalyst precursor for the direct arylation of 3-formylthiophene derivatives. When using 3-formylthiophene, the 2-arylated thiophenes were obtained with regioselectivities of 76–86%, whereas the arylation of 3-formylthiophene diethyl acetal gave the 5-arylated thiophenes with regioselectivities of 64–88%. These reactions were performed by using only 0.1 mol-% of the catalyst. Moreover, this procedure has been found to be tolerant to a variety of functional groups on the aryl bromide such as formyl, propionyl, benzoyl, nitrile, or nitro.

Introduction

Substituted thiophenes continue to attract the attention of synthetic organic chemists due to their inherent biological activity. Conventional methods for the synthesis of aryl thiophenes include metal-catalyzed cross-coupling reactions such as Suzuki-, Stille-, or Negishi-type reactions,[1] which permit the coupling of aryl halides with organometallic derivatives of thiophenes. Nevertheless, these procedures require the appropriate functionalization of one or both the coupling partners, and they produce stoichiometric amounts of metallic salts as byproducts. Moreover, when functionalized thiophene derivatives are employed, access to the corresponding organometallic derivatives might be tricky.

The direct coupling of functionalized thiophenes with aryl halides by C–H bond activation/functionalization should provide a cost-effective and environmentally attractive procedure for the preparation of functionalized aryl thiophenes. The selective C5 arylation of 2-substituted thiophenes by palladium-catalyzed C–H bond activation[2,3] has been largely described in recent years.[4] The polyarylation of 3-thiophenecarboxylic acid has been described by Miura and co-workers.[5] On the other hand, the regiocontrolled direct arylation of 3-substituted thiophenes has attracted less attention.[6–10] In 2003, Sharp and co-workers reported conditions that allow the selective regioselective arylation of methyl 3-thiophene carboxylate.[6] The use of $Pd(PPh_3)_4$ in toluene gave selectively the 2-arylated thiophene, whereas $Pd_2(dba)_3$ (dba = dibenzylideneacetone) in NMP (*N*-methyl-2-pyrrolidone) gave a mixture of 2- and 5-arylated thiophenes in a 15:51 ratio. Bilodeau and co-workers examined the regioselectivity of the arylation of 3-methylthiophene with bromobenzene by using $Pd[P(tBu)_3]_2$ as the catalyst. They obtained a mixture of the 2- and 5-phenylated thiophenes in a 3.3:1 ratio (30% yield of 2-phenylation and 9% yield of the 5-phenylated thiophene).[7] The direct arylation of 3-methoxythiophene has been explored by Borghese and co-workers.[8] With this reactant, 2-arylated thiophenes were regioselectively obtained in yields of 28–60%. In 1998, Lemaire and co-workers reported the direct arylation of 3-formyl-, 3-cyano-, and 3-nitrothiophene with aryl iodides.[9] In most cases, they obtained mixtures of 2-arylated and 2,4-diarylated thiophenes together with an important amount of homocoupling of the aryl iodide. For example, treatment of 3-formylthiophene with iodobenzene in the presence of $Pd(OAc)_2$ (8 mol-%), PPh_3 (16 mol-%), and K_2CO_3 as the base in DMF at 140 °C gave 2-phenyl-3-formylthiophene in 35% yield.[10]

In summary, to the best of our knowledge, the regioselective C2 arylation of 3-formylthiophene derivatives via palladium-catalyzed intermolecular C–H bond activation has been reported in moderate yields by using a high catalyst loading and only with iodobenzene. The direct C5 arylation of 3-formylthiophene has not been described. Thus, it would be useful to develop a simple procedure, employing low catalyst loadings and a variety of functionalized aryl bromides, allowing the direct arylation of 3-formylthiophenes to obtain either 2-aryl-3-formylthiophenes or 2-aryl-4-formylthiophenes in a regioselective manner.

Results and Discussion

We initially directed our efforts towards the palladium-catalyzed direct arylation of 3-formylthiophene with 4-bromobenzonitrile (Scheme 1, Table 1). The reaction was found to produce a mixture of **1a** and **1b** in a 79:21 ratio, using

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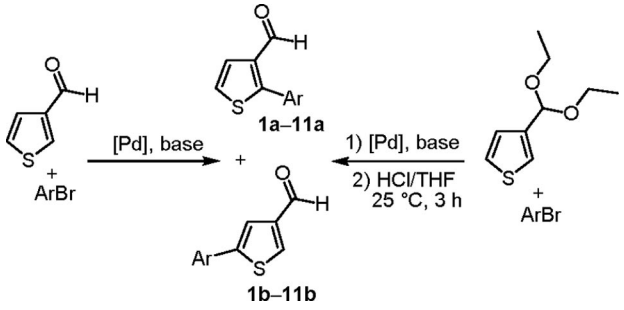
only 0.1 mol-% of $Pd(OAc)_2$ as the catalyst in the presence of KOAc as the base and DMAc (*N*,*N*-dimethylacetamide) as the solvent at 150 °C. In order to improve the regiocontrol of the arylation, we performed a series of experiments by using various solvents, bases, and catalysts. Bases exhibit a considerable difference of efficiency and regioselectivity for this reaction (Table 1, Entries 1–9). Carbonates or KF led to the formation of C2-arylated thiophene **1a** in lower regioselectivities than KOAc or NaOAc. The NMR spectra of the crude mixtures obtained by using KOAc were found to be cleaner than those obtained with the use of NaOAc. Next, we examined the influence of the solvent. The use of DMF or NMP resulted in low to moderate conversions of 4-bromobenzonitrile, and the regioselectivity of the arylation was not improved (Table 1, Entries 10 and 11). In the presence of xylene, coupling products **1a** or **1b** were not detected (Table 1, entry 14). The selectivity of the reaction was also slightly dependent on the catalyst. We observed that $[Pd(C_3H_5)Cl]_2$, in the absence of phosphane, exhibited high regioselectivity (80%) towards product **1a** (Table 1, Entry 19). Similar regioselectivities (80–81% of **1a**) were obtained in the presence of $Pd(OAc)_2$ associated to the phosphane ligands dppb [1,4-bis(diphenylphosphanyl)butane], dppe [1,2-bis(diphenylphosphanyl)ethane], dppf [1,1′-bis(diphenylphosphanyl)ferrocene], PPh_3, or PCy_3 (Table 1, Entries 12, 13, 15–18). GC and NMR analysis of the crude mixtures revealed that the reaction performed with $Pd(OAc)_2$ associated to dppb was very clean. With this catalyst, **1a** was isolated in 57% yield (Table 1, entry 13). Therefore, we selected this catalyst precursor to explore the scope and limitations of this reaction with the use of various aryl bromides.



Scheme 1.

3-Formylthiophene was coupled to a set of aryl bromides (Table 2). The reactions performed with *para*-substituted electron-deficient aryl bromides proceed conveniently in most cases. High regioselectivities in favor of C2 arylation were observed with the use of 4-bromobenzaldehyde, 4-bromopropiophenone, 4-bromobenzophenone, or 4-bromonitrobenzene, resulting in yields of 55–61% for products **2a**–**5a** (Table 2, Entries 2–5). *meta*-Substituted aryl bromide, 3-bromobenzonitrile gave **6a** in 58% yield (Table 2, Entry 6). A slightly lower regioselectivity in favor of C2 arylation was observed when *ortho*-substituted aryl bromides were employed. 2-Bromobenzaldehyde and 2-bromobenzonitrile gave mixtures of regioisomers **a/b** in 76:24 and 77:23 ratios, respectively (Table 2, Entries 7 and 8). This is certainly due to the steric hindrance of these aryl bromides. Pyridines or quinolines are π-electron deficient heterocycles, and therefore, their oxidative addition to palladium is, in general, relatively easy. 3-Bromopyridine and 3-bromoquinolines gave regioisomers **10a** and **11a** in regioselectivities of 83 and 82% (Table 2, Entries 10 and 11).

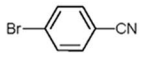
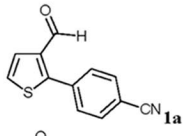
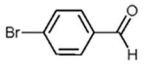
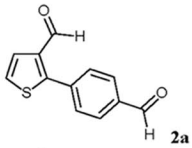
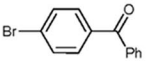
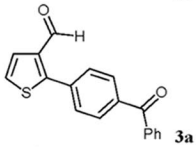
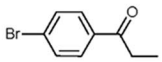
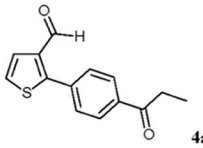
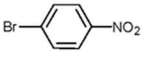
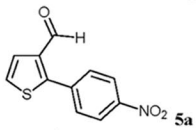
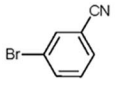
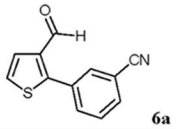
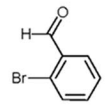
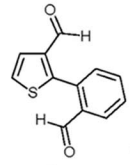
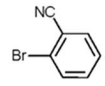
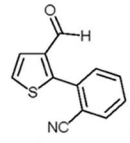
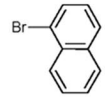
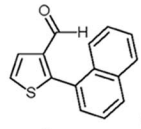
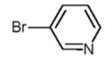
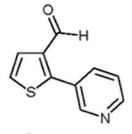
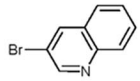
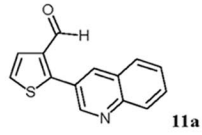
Next, we examined the reactivity of 3-formylthiophene diethyl acetal with 4-bromobenzonitrile (Scheme 1, Table 3). We employed a similar set of reaction conditions to those with 3-formylthiophene, and again, KOAc as the

Table 1. Arylation of 3-formylthiophene with 4-bromobenzonitrile: influence of the reaction conditions (Scheme 1).[a]

Entry	Solvent	Base	Catalyst	*T* [°C]	Conversion [%]	Ratio of **1a/1b**
1	DMAc	KOAc	$Pd(OAc)_2$	150	100	79:21
2	DMAc	KF	$Pd(OAc)_2$	130	70	69:31
3	DMAc	Cs_2CO_3	$Pd(OAc)_2$	130	50	mixture[b]
4	DMAc	Na_2CO_3	$Pd(OAc)_2$	130	52	72:28
5	DMAc	K_2CO_3	$Pd(OAc)_2$	130	82	62:38
6	DMAc	K_3PO_4	$Pd(OAc)_2$	130	2	trace
7	DMAc	NaOAc	$Pd(OAc)_2$	130	100	79:21
8	DMAc	KOAc	$Pd(OAc)_2$	130	76	78:22
9	DMAc	CsOAc	$Pd(OAc)_2$	130	100	71:29
10	DMF	KOAc	$Pd(OAc)_2$	130	55	75:25
11	NMP	KOAc	$Pd(OAc)_2$	130	20	mixture
12	DMAc	KOAc	$Pd(OAc)_2$/dppb[c]	130	100	81:19
13	DMAc	KOAc	$Pd(OAc)_2$/dppb[c]	150	100	81:19[e,f]
14	xylene	KOAc	$Pd(OAc)_2$/dppb[c]	130	0	–
15	DMAc	KOAc	$Pd(OAc)_2$/dppe[c]	130	100	80:20
16	DMAc	KOAc	$Pd(OAc)_2$/dppf[c]	150	100	80:20[e]
17	DMAc	KOAc	$Pd(OAc)_2/2PPh_3$[d]	130	100	81:19
18	DMAc	KOAc	$Pd(OAc)_2/2PCy_3$[d]	150	100	80:20[e]
19	DMAc	KOAc	0.5 $[Pd(C_3H_5)Cl]_2$	130	100	80:20

[a] Conditions: [Pd] (0.1 mol-%), 4-bromobenzonitrile (1 mmol), 3-formylthiophene (2 mmol), base (2 mmol), solvent (3 mL), 16 h; conversions and ratios of **1a/1b** determined by GC and NMR spectroscopy. [b] The formation of an important amount of biphenyl-4,4′-dicarbonitrile was observed. [c] 0.1 mol-% of diphosphane ligand. [d] 0.2 mol-% of PPh_3. [e] 3-Formylthiophene (1.5 mmol). [f] Isolated yield of **1a**: 57%.

Table 2. 2-Arylation of 3-formylthiophene with aryl bromides (Scheme 1).[a]

Entry	Aryl bromide	Major product	Ratio of **a**/**b**	% Yield of regioisomer **a**
1		 **1a**	81:19	57
2		 **2a**	85:15	55
3		 **3a**	84:16	56
4		 **4a**	86:14	58
5		 **5a**	85:15	61
6		 **6a**	80:20	58
7		 **7a**	76:24	44
8		 **8a**	77:23	48
9		 **9a**	80:20	52
10		 **10a**	83:17	54
11		 **11a**	82:18	50

[a] Conditions: $Pd(OAc)_2$ (0.1 mol-%), dppb (0.1 mol-%), aryl bromide (1 mmol), 3-formylthiophene (1.5 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 16 h; isolated yields of regioisomers **a**.

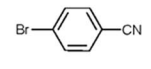
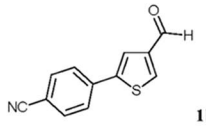
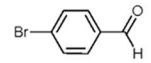
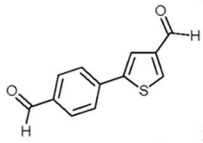
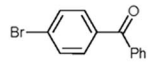
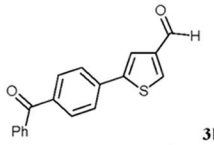
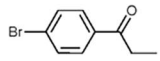
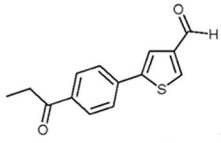
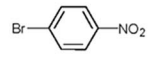
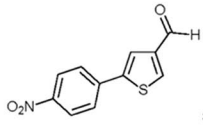
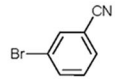
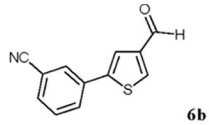
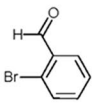
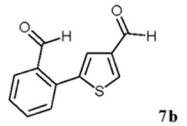
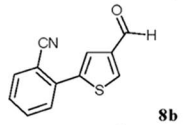
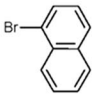
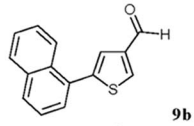
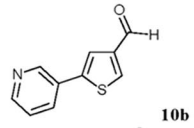
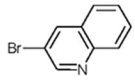
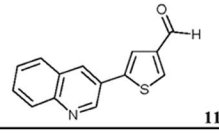
base was found to give a good conversion of the aryl bromide and also a quite regioselective arylation (Table 3, Entries 1–9). However, with this substrate, C5 arylation was predominant. The C2 carbon atom of 3-formylthiophene diethyl acetal is more hindered than the C2 carbon atom of 3-formylthiophene. The use of other solvents such as NMP

Table 3. Arylation of 3-formylthiophene diethyl acetal with 4-bromobenzonitrile, influence of the reaction conditions (Scheme 1).[a]

Entry	Solvent	Base	Catalyst	*T* [°C]	Conversion [%]	Ratio of **1a/1b**
1	DMAc	KOAc	$Pd(OAc)_2$	150	90	25:75
2	DMAc	KF	$Pd(OAc)_2$	130	30	28:72
3	DMAc	Cs_2CO_3	$Pd(OAc)_2$	130	8	24:76
4	DMAc	Na_2CO_3	$Pd(OAc)_2$	130	22	28:72
5	DMAc	K_2CO_3	$Pd(OAc)_2$	130	11	32:68
6	DMAc	K_3PO_4	$Pd(OAc)_2$	130	0	–
7	DMAc	NaOAc	$Pd(OAc)_2$	130	70	26:74
8	DMAc	KOAc	$Pd(OAc)_2$	130	77	23:77
9	DMAc	CsOAc	$Pd(OAc)_2$	130	80	29:71
10	DMF	KOAc	$Pd(OAc)_2$	130	80	24:76
11	NMP	KOAc	$Pd(OAc)_2$	130	82	25:75
12	DMAc	KOAc	$Pd(OAc)_2$/dppb[b]	130	100	27:73
13	DMAc	KOAc	$Pd(OAc)_2$/dppb[b]	150	100	24:76[d]
14	DMAc	KOAc	$Pd(OAc)_2$/dppe[b]	130	90	25:75
15	DMAc	KOAc	$Pd(OAc)_2/2PPh_3$[c]	130	90	24:76
16	DMAc	KOAc	0.5 $[Pd(C_3H_5)Cl]_2$	130	92	25:75

[a] Conditions: [Pd] (0.1 mol-%), 4-bromobenzonitrile (1 mmol), 3-formylthiophene diethyl acetal (2 mmol), base (2 mmol), solvent (3 mL), 16 h; conversions and ratios of **1a/1b** determined by GC and NMR spectroscopy. [b] 0.1 mol-% of diphosphane ligand. [c] 0.2 mol-% of PPh_3. [d] 3-Formylthiophene diethyl acetal (1.5 mmol), isolated yield of **1b**: 53%.

Table 4. 5-Arylation of 3-formylthiophene diethyl acetal with aryl bromides (Scheme 1).[a]

Entry	Aryl bromide	Major product	Ratio of a/b	% Yield of regioisomer b
1		 **1b**	24:76	53
2		 **2b**	24:76	48
3		 **3b**	22:78	50
4		 **4b**	24:76	48
5		 **5b**	28:72	53
6		 **6b**	28:72	55
7		 **7b**	12:88	40
8		 **8b**	17:83	62
9		 **9b**	13:87	51
10		 **10b**	36:64	42
11		 **11b**	30:70	40

[a] Conditions: 1) $Pd(OAc)_2$ (0.1 mol-%), dppb (0.1 mol-%), aryl bromide (1 mmol), 3-formylthiophene diethyl acetal (1.5 mmol), KOAc (2 mmol), DMAc (3 mL), 150 °C, 16 h; 2) HCl, THF, 25 °C 3 h. Isolated yields of regioisomers **b**.

or DMF did not improve the regioselectivity of the arylation (Table 3, Entries 10 and 11). Again, the cleanest NMR spectra of the crude mixtures were obtained by using $Pd(OAc)_2$/dppb as the catalyst precursor, KOAc as the base, and DMAc as the solvent at 150 °C (Table 3, Entry 13). Under these reaction conditions, the ratio of product **1a**/**1b** was 24:76, and the yield of **1b** was 53%.

Then, we explored the arylation of 3-formylthiophene diethyl acetal with several aryl bromides (Table 4). In the presence of aryl bromides electronically and sterically similar to 4-bromobenzonitrile, such as 4-bromobenzaldehyde, 4-bromobenzophenone or 4-bromopropiophenone, similar regioselectivities (76–78% of 5-arylation) and yields were obtained (Table 4, Entries 2–4). In contrast, when we employed a sterically congested aryl bromide, such as, 2-bromobenzonitrile, 2-bromobenzaldehyde, or 1-bromonaphthalene, the regioselectivities of the arylations in favor of regioisomers **7b**–**9b** were increased to 83–88% (Table 4, Entries 7–9). In the presence of 3-bromopyridine or 3-bromoquinoline, compounds **10b** and **11b** were obtained with a regioselectivity of 64 and 70%, respectively (Table 4, Entries 10 and 11).

Conclusion

In summary, we report herein a simple method for the preparation of 2-aryl-3-formylthiophenes or 2-aryl-4-formylthiophenes. We have demonstrated that the protection of the formyl function of 3-formylthiophene as an acetal dramatically modifies the regioselectivity of the arylation in favor of the coupling on the C5 carbon atom. This procedure requires the use of only 0.1 mol-% of the palladium catalyst and has proved to be tolerant to a variety of functional groups on the aryl bromide such as formyl, propionyl, benzoyl, nitrile, or nitro. No prior preparation of an organometallic derivative is required for these couplings, reducing the number of required steps to obtain these arylated thiophenes. Despite their interest, most of the products prepared by this method are new, indicating a relatively laborious access to such compounds by using more traditional cross-coupling procedures. Moreover, this reaction is environmentally attractive, as the major byproducts are AcOH/KBr instead of the metallic salts encountered with the use of more classical coupling procedures.

Experimental Section

General Procedure for the Reactions with 3-Formylthiophene: In a typical experiment, the aryl bromide (1 mmol), 3-formylthiophene (0.168 g, 1.5 mmol), and KOAc (0.196 g, 2 mmol) were introduced in an oven-dried Schlenk tube, equipped with a magnetic stirring bar. Then, $Pd(OAc)_2$ (0.22 mg, 0.001 mmol), dppb (0.42 mg, 0.001 mmol), and DMAc (3 mL) were added, and the Schlenk tube

was purged several times with argon. The Schlenk tube was placed in a preheated oil bath at 150 °C, and the reactants were allowed to stir for 16 h. The solvent was removed by heating the reaction vessel under vacuum, and the residue was charged directly onto a silica gel column.

General Procedure for the Reactions with 3-Formylthiophene Diethyl Acetal: Similar to the previous procedure, then, after cooling at room temperature, THF (5 mL) and HCl solution (pH 2, 5 mL) were added, and the mixture allowed to stir for 3 h. After separation and drying ($MgSO_4$), the solvent was removed under vacuum, and the residue was charged onto a silica gel column.

Supporting Information (see footnote on the first page of this article): General procedure for the reactions of 3-formylthiophene or 3-formylthiophene diethyl acetal with aryl bromides and characterization of **1a** and **1b**.

Acknowledgments

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