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Palladium-Catalyzed 2-Arylation of Pyrroles

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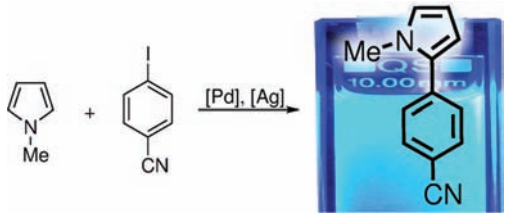

A methodology that affords *N*-alkyl-2-arylpyrroles and *N*-aryl-2-arylpyrroles via direct coupling from aryl iodides has been developed. After examining various reaction parameters: solvent, ratio of reagents, catalyst, base and additives the optimal conditions for the condensation were identified. Two crucial factors, (a) anhydrous DMSO as solvent and (b) 5 M excess of pyrrole counterpart, were found to strongly influence the reaction outcome. The conditions identified ($PdCl_2(PPh_3)_2$, AgOAc, anhyd DMSO, KF, 100 °C, 5 h) resulted in the formation of 2-arylpyrroles in 14−80% yield. Furthermore, the synthesis is compatible with electron-withdrawing and electron-donating groups on the aryl moiety.

Pyrroles are abundant in natural products[1] and medicinal agents[2] and serve as a number of intermediates in multistep syntheses.[3] They are also crucial building blocks in the synthesis of cyclic π-conjugated oligopyrrolic systems such as porphyrins[4] and other porphyrinoids.[5−9] Thus, many synthetic methods are known for the construction[10] and derivatization of pyrrole ring.[11]

Aryl-substituted pyrrole derivatives can be prepared via Suzuki coupling of *N*-substituted 2-bromopyrroles with boronic acids[12] or from *N*-protected pyrroleboronic acids esters and aryl bromides.[13] These strategies, however, cannot be applied to *N*-alkylpyrroles since bromo derivatives of these compounds lack an *N*-electron-withdrawing protecting group and hence are not stable. Such *N*-alkyl-2-arylpyrroles could be prepared via direct coupling as increased popularity of this method has been observed during the past few years.[14] In comparison to indole, only a few methods for direct arylation of pyrrole derivatives have been published. Intermolecular arylation of pyrrole reported by Filippini[15] (later optimized by Sadighi et al.[16]) requires the formation of an

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anion and subsequent transmetalation. Two other procedures (Sames'[17,18] and Fagnou's[19]) use complex rhodium and palladium catalysts and work only for limited range of substrates. Another method, recently developed by Sanford and co-workers, implies the use of noncommercially available I^{III} arylation agents.[20] Finally, Forgione, Bilodeau, and co-workers reported decarboxylative cross-coupling reaction between *N*-methylpyrrole-2-carboxylic acid and aryl bromides.[21]

Since the existing procedures are either expensive or noncomprehensive there is a need for the development of more general approach.[22] This prompted us to initiate the study aimed at developing conditions for direct coupling of *N*-alkylpyrroles with aryl halides.

Reactivity of pyrrole is similar to that of its benzo analogues indole and indolizine. Therefore, reaction conditions developed for indole served as a starting point of our study. The reaction of *N*-methylpyrrole (**1**) and 4-iodobenzonitrile (**2**) was chosen as a model system for the optimization studies (Scheme 1). Submitting these reagents to the conditions which work very well for arylation of indole[23,24] led to formation of *N*-methyl-2-(4-cyanophenyl)pyrrole (**3**) in poor yields. Another palladium-based system ($Pd(OAc)_2$, KOAc, PPh_3 in NMP) used for indolizine arylation employed by Gevorgyan[25] was also investigated without success.

Therefore, we investigated conditions developed for direct coupling of thiophene, reported by Lemaire and co-workers ($Pd(OAc)_2$, K_2CO_3, Bu_4NBr in CH_3CN).[26] However, the reaction gave only a small amount of product **3**. Finally, following Mori's procedure,[27] the mixture of *N*-methylpyrrole (**1**) and 4-iodobenzonitrile (**2**) was treated with $PdCl_2(PPh_3)_2$, $AgNO_3$, and KF in DMSO resulting in the formation of product **3** in 10% yield (Scheme 1, Table 1, entry 1). This initial success quickly led to the systematic study of the reaction conditions. The first set of experiments was carried out with $PdCl_2(PPh_3)_2$ to allow optimization of various parameters. In an effort to improve the yield of compound **3**, the solvent, ratio of reagents, silver salts, time, as well as other factors were altered. The results of this study are presented in Table 1.

The replacement of silver nitrate with silver acetate resulted in an increase in the yield to 20% (Table 1, entry 2). In contrast to DMSO, reactions in other solvents were sluggish and low yielding (Table 1, entries 3−8). The counterion of the silver salt was found to be crucial: AgOAc provided better yield of **3** in comparison to other salts (entries 9−10). Increasing the reaction temperature also did not improve the yield (entry 11). Replacement of DMSO with anhydrous DMSO increased the yield to 32% (entry 12). Mori et al. reported that the addition of silver nitrate in portions is crucial, presumably due to low stability of AgF. Our experiments confirmed this observation since the addition of AgOAc in one portion caused sudden decrease in the yield of product **3** (entry 13).

During the course of the reaction, 4,4′-dicyanobiphenyl (**4**) and bisarylated product **5** were formed in variable, albeit low yield depending on the specific conditions (Scheme 1); however, no 3-arylated product was found.

SCHEME 1

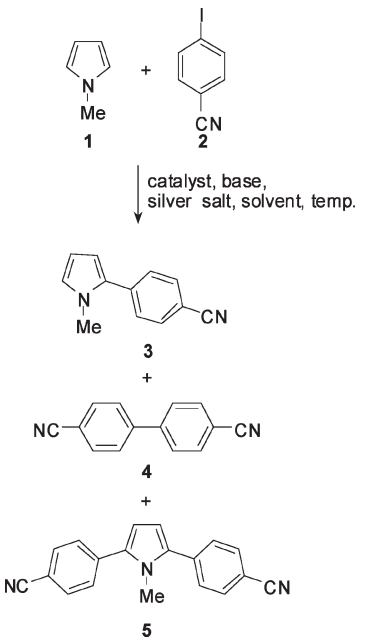

TABLE 1. Influence of the Reaction Conditions for the Coupling of *N*-Methylpyrrole (1) with 4-Iodobenzonitrile (2)[a]

entry	silver source	ratio **1**:**2**	solvent	yield of **3**[b] (%)
1	$AgNO_3$	1.2:1	DMSO wet	10
2	AgOAc	1.2:1	DMSO wet	20
3	AgOAc	1.5:1	MeCN	9
4	AgOAc	1.5:1	DMF	1
5	AgOAc	1.5:1	NMP	11
6	AgOAc	1.5:1	DMSO/dioxane	16
7	AgOAc	1.5:1	THF	0
8	AgOAc	1.5:1	AcOH	10
9	Ag_2CO_3	1.5:1	DMSO wet	0
10	AgOTf	1.5:1	DMSO wet	0
11[c]	AgOAc	1.5:1	DMSO wet	11
12	AgOAc	1.5:1	DMSO anhyd	32
13	AgOAc[d]	1.5:1	DMSO anhyd	16
14	AgOAc	2.5:1	DMSO anhyd	42
15	AgOAc	3.5:1	DMSO anhyd	66
16	AgOAc	5:1	DMSO anhyd	82

[a]All reactions were performed under following constant conditions: $PdCl_2(PPh_3)_2$ (5 mol %), KF (2 equiv), 5 h, addition of silver salt (altogether 1 equiv) in five equal portions every 1 h, 100 °C. [b]Yields were determined by HPLC. [c]Reaction was performed at 150 °C. [d]AgOAc was added in one portion.

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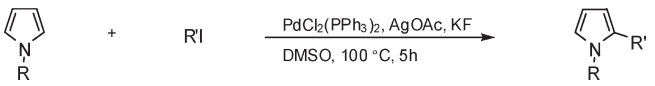
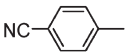
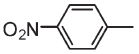
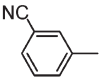
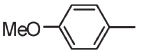
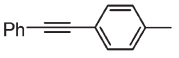
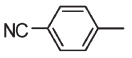
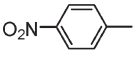
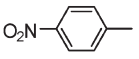
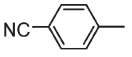
TABLE 2. Scope and Limitation Studies for Direct Arylation of Pyrrole Derivatives with Iodoarenes



Pyrrole	R	Aryl iodide	R'	Product	Yield
1	Me	2		3	80%
1	Me	9		15	73%
1	Me	10		16	70%
1	Me	11		17	30%
1	Me	12		18	30%
1	Me	13		19	14%
1	Me	14		20	55%
6		2		21	65%
6		9		22	59%
7		9		23	62%
8		2		24	53%

The ratio of compounds **1** and **2** was found to be the most important factor that influenced the yield of the formation of **3** (entries 14−16). Doubling the amount of compound **1** increased the yield by 10%. An additional increase of that ratio (to 5:1) led to 82% yield. Further attempts to improve the yield of **3** by changing the fluoride and the palladium source and incorporating a phosphine with a broad range of electron-donating abilities and steric effects did not lead to any improvement (see the table in the Supporting Information).

After establishing the optimum conditions (entry 16) for the desired transformation, the scope and limitations of this approach to synthesize broad range of 2-arylpyrroles was analyzed by testing a variety of iodoarenes with *N*-substituted pyrroles (Table 2). Aryl iodides with various substituents were reacted with *N*-methyl-, *N*-benzyl-, and *N*-phenylpyrrole leading to products **13**−**24** in yields ranging from 14% to 80%. Reaction with ortho-substituted aryl iodides **13** and **14** led to the desired products **19** and **20** albeit in lower yields (Table 2). In all cases, complete regioselectivity was observed. The reaction is more effective when an electron-withdrawing substituent is present on aryl iodide. When more complex aryl iodide **12** was used in the reaction with *N*-methylpyrrole (**1**), the desired product **18** bearing an ethynylphenyl moiety was obtained in moderate yield. In addition, 2-(pyrrol-1-ylmethyl)pyridine (**8**) subjected to reaction conditions led smoothly to product **24** (Table 2). Aryl bromides do not react under these conditions. The use of *N*-trimethysilylpyrrole did not lead to the desired arylation product (neither protected not unprotected). Surprisingly, the reaction also does not work for *N*-unsubstituted pyrrole. It is reasonable to assume that the mechanism analogous to that suggested previously,[28] i.e., oxidative addition of the palladium into the aryl iodide followed by electrophilic substitution, accounts for the formation of arylated pyrroles (however, other mechanisms also have to be taken into account).

In summary, direct coupling of aryl iodides with pyrrole derivatives provides a valuable method for the synthesis of *N*-alkyl-2-arylpyrrole and *N*-aryl-2-arylpyrrole derivatives. The relatively mild conditions and short reaction times are especially noteworthy compared to other related direct arylation of pyrrole.[21] Considering that starting materials are readily available the reaction may be deemed valuable. This approach should prove useful for the preparation of variety of derivatives and may open the door to exciting applications of these compounds. Further studies aimed at extending the scope of this method and gaining insight into spectroscopic properties of these products are in progress.

Experimental Section

General Procedure for Arylation of Pyrrole Derivatives. *N*-Substituted pyrrole (10 mmol, 5 equiv) was dissolved in a mixture of $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 5 mol %), KF (4 mmol, 2 equiv), and iodoarene (2 mmol, 1 equiv) in dry DMSO (2 mL). Subsequently, AgOAc (2 mmol, 1 equiv) was added in five portions every hour. The resulting suspension was stirred at 100 °C under Ar for 5 h. The reaction mixture was cooled to room temperature and poured into 50 mL of water. The precipitation was filtered through Celite and washed with dichloromethane. The organic layer was washed with water, and all water fractions were combined and extracted with toluene. Combined organic layers were dried (Na_2SO_4), filtered, and evaporated with silica under reduced pressure. The purification details are described for each case as follows.

***N*-Methyl-2-(4-cyanophenyl)pyrrole (3).** Following the general procedure, treatment of *N*-methylpyrrole (888 μL, 10 mmol) and 4-iodobenzonitrile (458 mg, 2 mmol) and further purification by dry column vacuum chromatography (DCVC) (EtOAc/hexanes, 0.5:99.5) afforded 289 mg (80%) of **3** (crystallized from Et_2O/pentane) as fine white crystals: R_f = 0.5 (silica, EtOAc/hexanes, 1:4); mp 102−103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.71 (s, 3H), 6.23 (t, 1H, J = 3.3 Hz), 6.34 (dd, 1H, J_1 = 3.6 Hz, J_2 = 1.7 Hz), 6.77 (t, 1H, J = 2.1 Hz), 7.49, 7.66 (AA′BB′, 2 × 2H, J = 8.4 Hz); ^{13}C NMR (500 MHz, $CDCl_3$) δ 35.4, 108.5, 109.7, 110.7, 118.9, 125.8, 128.3, 132.2, 132.6, 137.7; EI-MS HR obsd 182.0833 [M^+], calcd exact mass 182.0844 ($C_{12}H_{10}N_2$). Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.03; H, 5.51; N, 15.33.

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***N*-Phenyl-2-(4-nitrophenyl)pyrrole (22).** Following the general procedure, treatment of *N*-phenylpyrrole (1.43 g, 10 mmol) and 4-iodonitrobenzene (498 mg, 2 mmol) and further purification by DCVC (hexanes) afforded 314 mg (59%) of **22** (crystallized from CH_2Cl_2) as fine yellow crystals: R_f = 0.64 (silica, EtOAc/hexanes, 1:4); mp 130−131 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (dd, 1H, J_1 = 3.7 Hz, J_2 = 2.8 Hz), 6.63 (dd, 1H, J_1 = 3.7 Hz, J_2 = 1.7 Hz), 7.02 (dd, 1H, J_1 = 2.8 Hz, J_2 = 1.7 Hz), 7.18 (dt, 2H, J_1 = 6.8 Hz, J_2 = 1.6 Hz), 7.22, 8.04 (AA′BB′, 4H, J = 9.1 Hz), 7.37 (m, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 110.1, 113.3, 126.6, 125.7 126.9, 127.4, 127.8, 129.4, 131.4, 139.2, 139.9, 145.6; EI-MS obsd 264.0890 [M^+], calcd exact mass 264.0899 ($C_{16}H_{12}N_2O_2$). Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58, N, 10.60. Found: C, 72.74; H, 4.54; N, 10.67.

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Supporting Information Available: Full description of experimental procedures and analyses of compounds **15**−**24**. ^{1}H NMR and ^{13}C NMR spectra for compounds **3**−**5** and **15**−**24**. This material is available free of charge via Internet at http://pubs.acs.org.