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C–H Activation

AgONO-Assisted Direct C–H Arylation of Heteroarenes with Anilines

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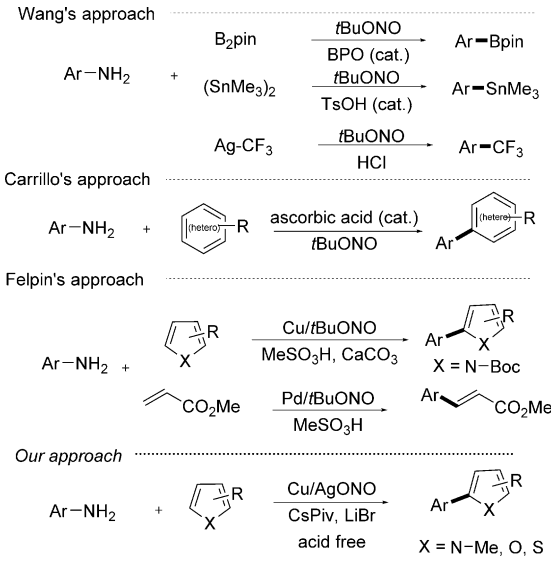
Abstract: A novel copper-catalyzed C–H arylation of heteroarenes with anilines by an in situ diazonium reaction is established by using silver nitrite (AgONO) as an unconventional nitrosating reagent under acid-free conditions. It provides a complementary approach for the C–H arylation of electron-rich heteroarenes with aromatic amines affording a variety of heterobiaryls in moderate to good yields.

Heterobiaryls are extremely important motifs in biologically active molecules, natural products, and materials chemistry. Their synthesis by direct arylation[1] and oxidative coupling[2] through C–H activation has attracted great interest in both academia and industry lately. From a green chemistry perspective, these methods are regarded as highly advantageous over the traditional cross-coupling methods due to the elimination of the need of prefixing and subsequent removal of reactive functionalities, hence leading to a decrease in the number of steps in a given synthesis and thereby minimizing the use and generation of stoichiometric amounts of hazardous chemicals.

The use of aryl diazonium salts as surrogate electrophiles for cross-coupling reactions has been receiving increased attention recently,[3] as they are highly reactive, act as a source of aryl radicals, and are readily accessible from anilines that are ubiquitous and inexpensive compared to aryl halides and triflates. The C–H arylation by using diazonium salts was known as early as the 1900s, as in the case of Meerwein C–H arylation,[4] Pschorr's cyclization,[5] and Gomberg–Bachmann biaryl synthesis.[6] However, application of these reactions were restricted because of the poor selectivity and substrate scope in addition to the difficulty in isolating and handling the highly unstable and potentially explosive diazonium salts in their crystalline form. Nevertheless, further research in this area showed substantial promise. The problem of the instability of the diazonium salts was fairly addressed by developing more stable diazonium salts with BF_4^-, PF_6^-, and OTs^- as counter ions[7] and was applied as safer alternatives in various C–C coupling reactions including C–H arylation. For instance, Sanford et al.[8] demonstrated a directing-group-assisted mild arylation of aromatic C–H bonds with aryl diazonium tetrafluoroborates by merging Pd-catalyzed C–H activation and Ru-based visible-light photoredox catalysis. König and co-workers independently reported[9] a metal-free variation for the direct C–H arylation of heteroarenes by using Eosin Y as the photoredox catalyst with aryl diazonium tetrafluoroborates.

Alternatively, in situ generation of diazonium salts would elude any erratic safety issues in using prior isolated diazonium salts. In this regard *tert*-butylnitrite (*t*BuONO) has been proposed as an efficient in situ diazotization reagent.[10] Thus, recent studies showed that aniline can be directly converted to aryl boronates,[11] aryl-Sn,[12] aryl-CF_3,[13] aryl-N_3,[14] aryl olefins,[15] and aryl heteroarenes[16] through in situ diazonium reactions by using *tert*-butylnitrite (Scheme 1). Recently, Felpin et al.[16] developed a copper-catalyzed Meerwein C–H arylation of pyrroles by in situ generated diazonium salts using *t*BuONO. However, this approach was limited to *N*-Boc-pyrroles. In the case of electron-rich pyrroles, only an unwanted azo product was isolated. Very recently, Martin, Carrillo, and co-workers demonstrated[17] a similar in situ diazonium-based reaction using *t*BuONO in combination with ascorbic acid as a free radical initiator towards a metal-free direct C–H arylation of arenes, particularly furans.



Scheme 1. New transformations of aniline by an in situ diazotization reaction.

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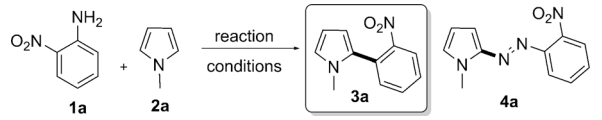
We report herein a general copper-catalyzed direct C–H arylation of electron-rich heterocycles including *N*-methylpyrroles, furans, and thiophenes by using anilines in the presence of silver nitrite (AgONO) as an alternative diazotization agent under acid-free conditions. To the best of our knowledge, this is the first example on the use of AgONO as a diazotization agent. While AgONO has commonly been used as a nitration reagent[18] and oxidant,[19] its synthetic applicability as a nitrosating agent has never been evaluated in diazonium chemistry. AgONO is relatively safer to use at elevated temperatures than *t*BuONO, which is highly flammable, may readily decompose, and explodes on heating.[20] Moreover, there are only a few reports on diazotization reactions under acid-free conditions.[11,21] Our discovery was based on a recent study[22] in our lab on the Rh^{III}/aniline dual catalysis for the oxidative coupling of aldehydes by *ortho* C–H activation. While examining different oxidants and solvents for this reaction, we coincidentally observed the formation of traces of biaryl side products, resulting from a Gomberg–Bachmann-type reaction of the aniline with the solvent benzene when AgONO was used as the oxidant. Inspired by this observation, we set out to investigate the possibility of using AgONO as an in situ diazotization reagent in the Meerwein-type arylation of heteroarenes with anilines.

We selected the challenging electron-rich *N*-methylpyrrole (**2a**) as the model heteroarene substrate for our initial investigations as it was poorly active towards C–H arylation when using the prior methods by diazonium chemistry and was not well explored.[9,16,17] Accordingly, the reaction of **2a** with 2-nitroaniline in the presence of *t*BuONO, using the reported[16] catalyst system $Cu(OAc)_2$/$MeSO_3H$/$CaCO_3$ resulted merely in the formation of the diazo product 1-methyl-2-[(2-nitrophenyl)diazenyl]-1*H*-pyrrole (**4a**) (Table 1, entry 1) with no detectable C–H arylation. We then studied the possibility of employing AgONO as the nitrosating agent for this reaction using $Cu(OAc)_2$ as the catalyst along with acetic acid (AcOH) or pivalic acid (PivOH) as acid additives to facilitate diazotization as well as C–H activation. We were delighted to find that these reactions resulted in significant C–H arylation forming 1-methyl-2-(2-nitrophenyl)-1*H*-pyrrole (**3a**) (Table 1, entries 4 and 5) selectively at 90 °C, although there was no conversion of the substrates at room temperature. Furthermore, to our surprise, we discovered that the desired product **3a** could be attained in 46% yield even in the absence of any acid additives (entry 6). We then examined different copper catalysts under these conditions, but no significant improvement in the performance was observed (entries 7–10). A control reaction in the absence of any copper catalyst showed no reaction (entry 11). Subsequently, to improve the yield further, other additives were explored. The addition of bases, such as Cs_2CO_3, K_2CO_3, and $CaCO_3$, was not beneficial (entries 12–14). Interestingly, additives, such as LiBr, AgCl, and CsOPiv, showed improvement in the yield of **3a**, reaching up to 62% in the case of LiBr (entry 17). Finally, adding 0.1 equivalents of CsOPiv along with LiBr further improved the yield to 67% (entry 18). When the reaction time was shortened to 8 h, the yield was reduced to 54% (entry 19). Moreover, when *t*BuONO was used instead of AgONO under these conditions, the yield of **3a** (9%) dropped dramatically, which indicated the significance of AgONO for this C–H arylation (entry 20). It is noteworthy that this reaction worked well under neat conditions, rather than in the presence of any solvents (entries 21 and 22). The excess amount of the heteroarene aided in suppressing the side product nitrobenzene formed by reductive deamination.

Table 1. Optimization studies on the C–H arylation of *N*-methyl pyrrole with 2-nitroaniline.



Entry	Catalyst	Additive (equiv)	*T* [°C]	Yield **3a** [%][a,b,c]
1[d]	$Cu(OAc)_2$	$MeSO_3H$/$CaCO_3$ (1.0)	RT	–
2	$Cu(OAc)_2$	CH_3COOH (1.0)	RT	–
3	$Cu(OAc)_2$	PivOH (1.0)	RT	–
4	$Cu(OAc)_2$	CH_3COOH (1.0)	90	23
5	$Cu(OAc)_2$	PivOH (1.0)	90	42
6	$Cu(OAc)_2$	–	90	46
7	CuOAc	–	90	42
8	$CuCl_2$	–	90	44
9	Cu_2O	–	90	28
10	$CuSO_4 \cdot 5H_2O$	–	90	30
11	–	–	90	–
12	$Cu(OAc)_2$	Cs_2CO_3(1.0)	90	18
13	$Cu(OAc)_2$	K_2CO_3(1.0)	90	13
14	$Cu(OAc)_2$	$CaCO_3$ (1.0)	90	32
15	$Cu(OAc)_2$	CsOPiv (0.5)	90	59
16	$Cu(OAc)_2$	AgCl (0.5)	90	49
17	$Cu(OAc)_2$	LiBr (0.5)	90	62
18	$Cu(OAc)_2$	LiBr(0.5)/CsOPiv(0.1)	90	67
19[e]	$Cu(OAc)_2$	LiBr(0.5)/CsOPiv(0.1)	90	54
20[f]	$Cu(OAc)_2$	LiBr(0.5)/CsOPiv(0.1)	90	9
21[g]	$Cu(OAc)_2$	LiBr(0.5)/CsOPiv(0.1)	90	39
22[h]	$Cu(OAc)_2$	LiBr(0.5)/CsOPiv(0.1)	90	28

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (10.0 mmol), catalyst (0.3 mmol), AgONO (1.2 mmol), 90 °C, 12 h. [b] The yield was measured by ^1H NMR spectroscopic analysis of the crude reaction mixtures by using CH_2Br_2 as the internal standard. [c] Traces of **4a** and nitrobenzene were detected by GCMS. [d] *t*BuONO (1.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.3 mmol), acetone/H_2O, 12 h.[16] [e] 8 h. [f] *t*BuONO instead of AgONO, 8 h. [g] *N*-methylpyrrole (3.0 mmol)/acetone (1 mL). [h] *N*-methylpyrrole (3.0 mmol)/DMSO (1 mL).

With the optimal conditions in hand, we examined the scope of this method for the direct C–H arylation of *N*-methylpyrrole with different substituted aryl amines (Scheme 2). In all these cases, the corresponding C2-arylated pyrrole derivatives **3a–m** were formed with high selectivity and moderate to good isolated yields (35–81%). In general, electron-poor anilines performed better than their electron-rich counter partners and a range of functional groups (NO_2, COOMe, CN, COMe, CF_3, Br, Cl, and OH) were tolerated. Notably, bromo- and chloro-substituted aniline (**3c** and **3j–l**) successfully underwent the coupling reaction intact with the C–Br/C–Cl bond, which will be useful for further functionalization. The heteroarylation of *N*-methylpyrrole with isoquinoline-1-amine produced 1-(1-methyl-1*H*-pyrrol-2-yl)isoquinoline (**3m**) in 20% isolated yield. The 2-substituted pyrrole derivatives, such as 1-(1-methyl-1*H*-pyrrol-2-yl)ethan-1-one and 1-(1*H*-pyrrol-2-yl)ethan-1-one, also

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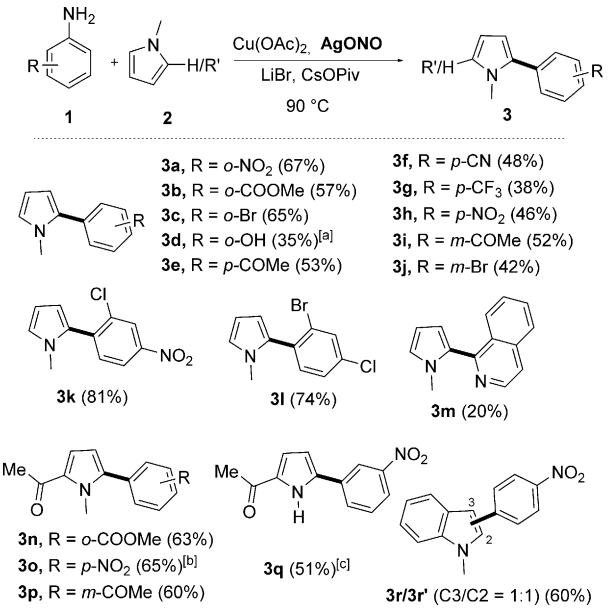
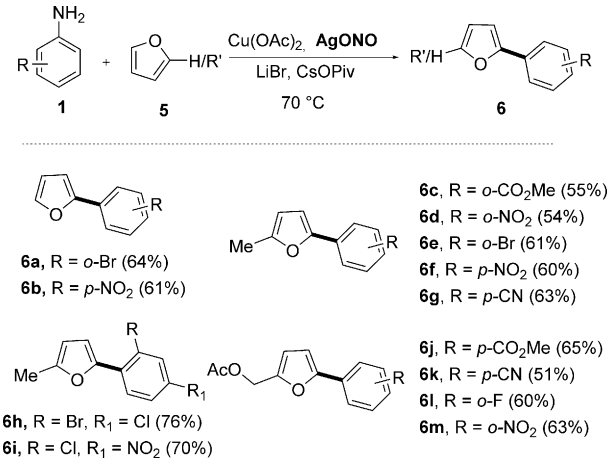


Scheme 2. C–H arylation of pyrroles and indoles with anilines. Reaction conditions: **1** (1.0 mmol), **2** (10.0 mmol or 1 mL), $Cu(OAc)_2$ (0.3 mmol), AgONO (1.2 mmol), CsOPiv (0.1 mmol), LiBr (0.5 mmol), 90 °C, 12 h. The yields given are isolated yields. Complete conversion of anilines was observed by TLC and GCMS analysis. [a] At room temperature. [b] Isolated along with the corresponding C3-arylated product in a ratio of 9.1:1 [c] *N*-methylpyrrole (3.0 mmol)/acetone (1 mL) at 60–70 °C.

gave the corresponding C5-arylated products (**3n–q**) selectively in moderate yields (43–65%). Under these conditions, *N*-methylindole furnished a 60% yield of the corresponding C3- (**3r**) and C2-arylated (**3r'**) products in a ratio of 1:1.

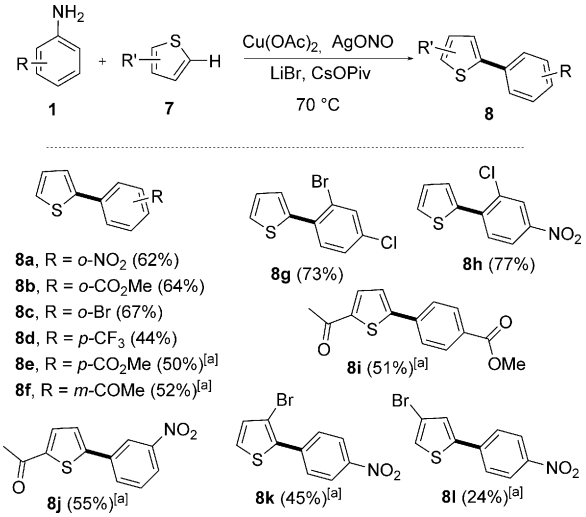
Next, the C–H arylation of furan as well as the hitherto less explored electron-rich C2-substituted furan derivatives, such as 2-methylfuran and furan-2-ylmethyl acetate, with different anilines were investigated (Scheme 3). Remarkably, in all these cases, the reaction was completed in 8 h at 70 °C, affording the



Scheme 3. C–H arylation of furans with anilines: Reaction conditions: aniline (1.0 mmol), furan (10.0 mmol or 1 mL), $Cu(OAc)_2$ (0.3 mmol), AgONO (1.2 mmol), CsOPiv (0.1 mmol), LiBr (0.5 mmol), 70 °C, 8 h. The yields given are for the isolated product. Complete consumption of anilines was observed by TLC and GCMS analysis.

corresponding C2- or C5-arylated products with high selectivity. It is noteworthy that under the conditions reported herein, C–H arylation always occurred selectively at the C2-position on the simple furan and C5-position on the C2-substituted furan with no detectable byproducts arising from C–H arylation at the other positions. Similar to the case of the pyrroles, the reaction occurred smoothly with various *ortho*-, *meta*-, and *para*-substituted anilines, particularly with electron-withdrawing groups, giving moderate to good yields (51–76%) of the corresponding arylfuran derivatives (**6a–m**).

Further usefulness of this methodology was demonstrated by the successful C–H arylation of thiophenes. Under similar conditions to that of furans, the coupling reaction of various thiophene derivatives and anilines took place efficiently to afford the corresponding aryl thiophenes **8a–l** in moderate to good yields (24–77%; Scheme 4). However, in cases for which there are two possible reactive sites, as in the case of the unsubstituted thiophene, a minor amount of the C3-arylated product was also formed.



Scheme 4. C–H arylation of thiophenes with anilines: Reaction conditions: aniline (1.0 mmol), thiophene (10.0 mmol or 1 mL), $Cu(OAc)_2$ (0.3 mmol), AgONO (1.2 mmol), CsOPiv (0.1 mmol), LiBr (0.5 mmol), 70 °C, 8 h. The yields given are total isolated yields of the two regioisomers. Complete conversion of anilines was observed by TLC and GCMS analysis. [a] Only the C2-arylated product was observed.

Our preliminary mechanistic investigations on this novel C–H arylation by using aniline in the presence of AgONO suggests a radical mechanism analogous to that proposed by Felpin et al.[16] When 2-nitroaniline (**1a**) or 2-aminomethyl benzoate (**1b**) and AgONO were reacted in the presence of the radical scavenger 2,2,6,6-tetramethyl-1-piperidin-1-oxyl (TEMPO), the corresponding *O*-aryl-TEMPO adducts (**10a** and **10b**) were trapped and detected by GCMS analysis (Scheme 5a) confirming the generation of the corresponding aryl radicals. Interestingly, we have also isolated and characterized a *C*-nitroso pyrrole adduct **11** by the reaction of **1b** with *N*-methylpyrrole (Scheme 5b), which perhaps is formed by the reaction of the radical intermediate **III-b** with AgONO.[23] Thus,

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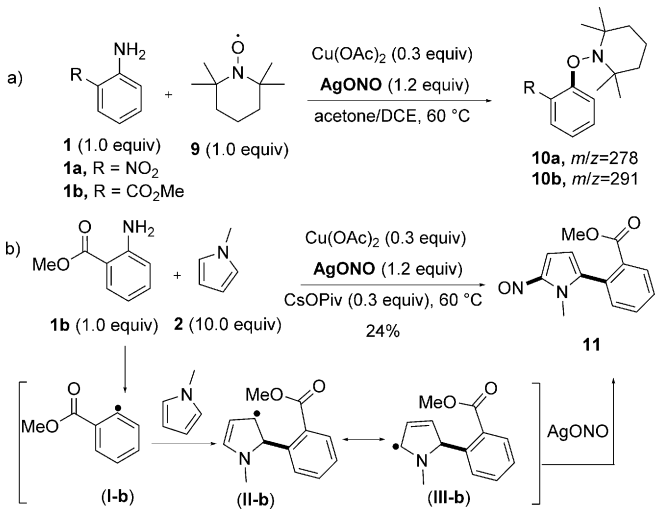

Scheme 5. Mechanistic studies.

the catalytic cycle involves a Cu^{I}-mediated homolytic dediazoniation of the in situ generated aryldiazonium salt, from the aniline and AgONO, affording the aryl radical **I**, which is rapidly captured by the heteroarene forming the radical intermediate **II**. The Cu^{II} catalyst then oxidizes the radical intermediate **II** to the heterobiaryl products (**3**, **6**, and **8**) by regenerating the active Cu^{I} species. Nevertheless, further studies are necessary to understand the complete mechanism.

Conclusion

We have developed a copper-catalyzed method for the C–H arylation of heteroarenes with anilines by an in situ diazonium reaction using silver nitrite as an unusual nitrosating agent under acid-free conditions. The C–H arylation proceeds smoothly at 70–90 °C, and displays a broad substrate scope towards electron-rich pyrroles, furans, and thiophenes with excellent functional-group tolerance. Further studies directed towards understanding the mechanism of this reaction and extending the application of this AgONO-based in situ diazonium reaction for other coupling reactions are underway.

Experimental Section

General procedure for the C–H arylation

An oven-dried 8 mL reaction vial was charged with $Cu(OAc)_2$ (54 mg, 0.3 mmol, 30 mol%), AgONO (185 mg, 1.2 mmol), LiBr (43 mg, 0.5 mmol), CsOPiv (24 mg, 0.1 mmol), aniline (1.0 mmol), and the heteroarene (10.0 mmol) in open air. The vial was sealed with a septum and the reaction mixture was stirred at 70–90 °C for 8–12 h. The crude reaction mixture was filtered through a pad of magnesium sulfate, the filtrate concentrated under reduced pressure and the crude product was purified by flash chromatography.

Acknowledgements

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Keywords: C–H arylation · copper acetate · diazonium reaction · heteroarenes · silver nitrite

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