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Organocatalytic, Oxidative, Intermolecular Amination and Hydrazination of Simple Arenes at Ambient Temperature

Rajarshi Samanta,[†] Jonathan O. Bauer,[‡] Carsten Strohmann,[‡] and Andrey P. Antonchick*,[†]

Max-Planck-Institut für Molekulare Physiologie, Abteilung Chemische Biologie, Otto-Hahn-Strasse 11, 44227 Dortmund, Germany, and Technische Universität Dortmund, Fakultät Chemie, Anorganische Chemie, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany

andrey.antonchick@mpi-dortmund.mpg.de

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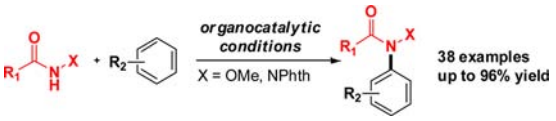
ABSTRACT



New atom-economical, environmental friendly, direct oxidative intermolecular processes of amination and hydrazination of nonprefunctionalized arenes were developed. The products were formed in a good regioselective manner under organocatalytic conditions at ambient temperature.

Efficient environmentally benign methods for product synthesis from easily available feedstock are in great demand. Over the past decades, varieties of processes have been developed for the coupling of prefunctionalized building blocks in high yields and with predictable regioselectivity.[1,2] The development of direct methods of C−H bond functionalization provided a powerful tool for organic synthesis. Despite the tremendous progress in transition metal catalyzed C−H bond functionalization, significant challenges still remain. In order to enhance the utility of C−H bond functionalization, the development of methods that proceed at ambient temperature devoid of transition metal catalysts and metal containing oxidants are highly desired.[2] Metal-free, moreover organocatalytic methods of direct C−H functionalization are very beneficial. The development of mild methods of oxidative cross-coupling of nonfunctionalized arenes is highly demanded. Herein, we report the development of an oxidative, environmentally benign method of amination and hydrazination of nonprefunctionalized arenes at ambient temperature under organocatalytic reaction conditions.[3]

Intermolecular amination of arenes is of immense interest due to the prevalence of C−N bonds in pharmaceuticals and natural products. The catalytic methods reported so far for intermolecular amination are based predominantly on transition metal catalysis.[4] Activated systems such as azoles or polyfluorinated systems have been studied extensively.[5] There are only a handful of examples reported in the literature for the transition metal catalyzed directed amination of nonfunctionalized arenes.[6] Synthetic strategies that afford the direct, atom economic formation of C−N bonds from unactivated substrates are highly desired.

[†] Max-Planck-Institut für Molekulare Physiologie
[‡] Technische Universität Dortmund

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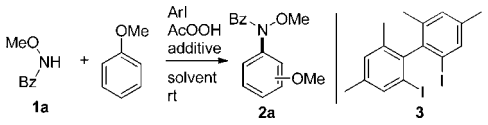
Recently, we developed an intermolecular, metal-free, direct oxidative method of C−N bond formation via cross-coupling of nonprefunctionalized arenes mediated by a hypervalent iodine[7] reagent.[3a] The products were obtained regioselectively at ambient temperature. Nevertheless, electron-poor arenes were not reactive under the developed reaction conditions. Simultaneously, Chang et al.[8a] and DeBoef et al.[8b] reported similar transformation using the same reagent. Interestingly, conducting the reaction at higher temperature allowed functionalization of electron poor arenes. The application of higher temperature required increased amounts of reagent due to low thermostability of (diacetoxy)iodobenzene and resulted in nonregioselective formation of aminated products. Inspired by the possibilty of functionalization of C−H bonds under metal-free conditions via cross-amination, we were motivated to develop mild organocatalytic conditions.[9] We envisaged that application of nitrenium cations stabilized by a heteroatom could provide an access to cross-amination.[10,11] The stabilized nitrenium ions could be obtained under catalytic conditions using aryliodide as catalyst. The reactive iodine(III) species would be generated by in situ oxidation of aryl iodide with peracetic acid.[12,13] Herein, we describe the realization of C−H bond functionalization of arenes under organocatalytic conditions.

We began our studies using *N*-methoxybenzamide (**1a**) as amination reagent for the functionalization of anisole (Table 1). A variety of aryl iodides were screened in presence of peracetic and trifluoroacetic acid in order to obtain the desired product (**2a**) in good yield and regioselectivity (Table 1, entries 1−4). The application of substoichiometric amounts of iodobenzene provided the target product in 62% yield with the major *ortho* regioisomer over the corresponding *para* regioisomer in 5:1 ratio (Table 1, entry 1). Electron rich 4-iodotoluene provided a slightly better yield compared to iodobenzene, whereas

Table 1. Optimization of the Organocatalytic Cross Amination[a]



entry	ArI (mol %)	solvent	time [h]	yield [%][b]	*o*:*p*[c]
1	PhI (20)	$CHCl_3$	6	62	5:1
2	4-MeC_6H_4I (20)	$CHCl_3$	4	71	3:1
3	4-FC_6H_4I (20)	$CHCl_3$	7	50	4:1
4	**3** (10)	$CHCl_3$	3	82	2.5:1
5	**3** (10)	CH_2Cl_2	3.5	76	3:1
6	**3** (10)	CCl_4	3.5	62	3:1
7	**3** (10)	DCE	3.5	76	6:1
8[d]	**3 (10)**	**DCE**	**2**	**69**	**6:1**
9[e]	**3** (10)	DCE	7	93	3.5:1
10[d,f]	**3** (10)	DCE	4	50	5:1
11[d,g]	**3** (10)	DCE	4	62	6:1
12[d,h]	**3** (10)	DCE	3	nd	nd

[a] Conditions: **1a** (1 equiv), anisole (10 equiv), ArI, AcOOH (2.2 equiv), trifluoroacetic acid (5 equiv) in solvent (0.2 M). [b] Isolated yields. [c] Ratio measured by ^{1}H NMR [d] Anisole (2 equiv) was used. [e] Reaction conducted at 0 °C. [f] CF_3CO_2H used (2.5 equiv). [g] AcOOH used (3 equiv). [h] Without CF_3CO_2H. Bz = benzoyl group, DCE = 1,2 dichloroethane, nd = not determined.

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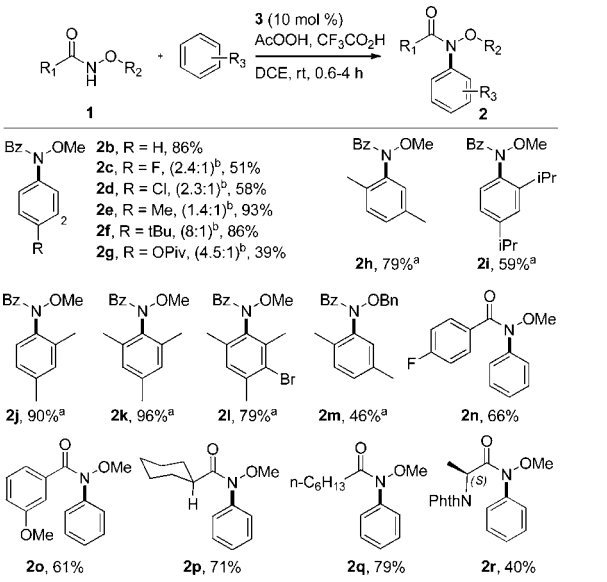
electron poor iodoarenes such as 4-fluoroiodobenzene led to formation of **2a** in lower yield (Table 1, entries 2, 3). To our delight, we found that iodoarene **3**[12] catalyzed the intermolecular amination at lower catalyst loading, resulting in shorter reaction time and better yield of **2a** (Table 1, entry 4). It is notable that successful intermolecular transformations using catalyst **3** have never been described to the best of our knowledge. Afterward, various solvents were tested (Table 1, entries 4–7). We could increase the regioselectivity of **2a** toward *ortho* over *para* in 6:1 ratio by optimization of the solvent (Table 1, entry 7). Notably, use of THF, MeCN, $MeNO_2$, MeOH was not successful. Gratifyingly, substantial decrease of arene amount to 2 equiv led to the desired product in impressive yield (69%) with the same regioselectivity (Table 1, entry 8). When the reaction was performed at 0 °C, **2a** was obtained with a better yield (93%) but regioselectivity was reduced (Table 1, entry 9). Decrease of trifluoroacetic acid amount or increase of peracetic acid amount provided the product in lower yield (Table 1, entries 10, 11). The formation of the desired product was not observed in absence of trifluoroacetic acid (Table 1, entry 12). With exception of trifluoroacetic acid, utilization of other additives such as triflic acid, boron trifluoride, trimethylsilyl triflate did not provide the desired product.

After optimizing the method for the organocatalytic, oxidative intermolecular amination at ambient temperature, we focused on the exploration of the scope and generality of the method. At first, benzene and monosubstituted benzene derivatives were examined (Scheme 1, products **2b**–**2g**). We were pleased to find that simple benzene also can be aminated in this process with 86% yield (Scheme 1, product **2b**). Even electron poor arenes like chlorobenzene, fluorobenzene were functionalized using this developed mild method with modest yield and *para*-regioselectivity (Scheme 1, product **2c**, **2d**). The application of electron-rich arenes led to a yield of up to 93% (Scheme 1, product **2e**). Notably, replacement of the methyl group to pivaloyl at the oxygen atom of phenol led to a switch in regioselectivity of amination (Table 1, entry 8 and Scheme 1, product **2g**). Polysubstituted benzene derivatives smoothly react giving desired products in 59–96% yield (Scheme 1, products **2h**–**2l**). Afterward, having in hand a wide range of aminated arenes with *N*-methoxy benzamide, we tested various amination reagents (Scheme 1, products **2m**–**2r**). In general, we found that the presence of substituents with different electronic and steric properties did not have exceptional effect on

Scheme 1. Scope of Amination of Arenes



Reaction conditions: **1a** (1 equiv), arene (20 equiv), **3** (10 mol %), AcOOH (2.2 equiv), CF_3CO_2H (5 equiv), in DCE (0.2 M). Yields are given for isolated products after column chromatography. Newly formed bonds are shown in bold. [a]Arene (2 equiv) used. [b]The minor regioisomeric position is labeled with the respective carbon atom number. Ratio of regioisomeric products was measured by weight of isolated product.

the formation of intermolecular C–N bonds. Finally, the developed organocatalytic protocol allows functionalization of arenes by amino acid derivatives in modest yield (Scheme 1, product **2r**). It is notable that only products of monoamination were selectively obtained under the developed reaction conditions. The obtained *N*-methoxy-*N*-phenylbenzamide derivatives **2** represent a common scaffold for bioactive compounds and useful products for the synthesis of nitrogen-containing derivatives (see the Supporting Information for details).

After successful development of the intermolecular amination process, we looked for organocatalytic hydrazination of nonprefunctionalized arenes. Notably, intermolecular cross-coupling of hydrazine derivatives and nonprefunctionalized arenes had not been reported earlier to the best of our knowledge. We were pleased to find that in an initial test reaction under the developed organocatalytic conditions, the *N*-(1,3-dioxoisoindolin-2-yl)acetamide (**4**) reacted smoothly with benzene to give the cross hydrazinated product at ambient temperature in 92% yield (Scheme 2, product **5a**). Afterward, we focused on investigation of the generality of the discovered organocatalytic cross-hydrazination. Cross hydrazination worked uninterruptedly with monosubstituted benzenes in good to excellent yields (Scheme 2, product **5b**–**5l**). The sterically bulky reagent **4** forced the *para* selectivity during organocatalytic hydrazination. The yield and regioselectivity of *para*-isomers were increased from fluorobenzene to iodobenzene (Scheme 2, products **5f**–**5i**). Arenes that are challenging and sensitive to nucleophiles, such as *N*-phenyl succinimides, were functionalized under organocatalytic

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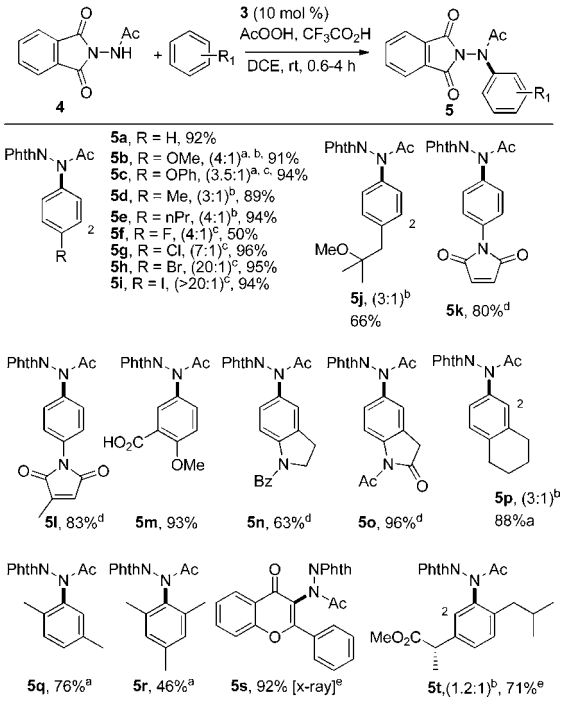
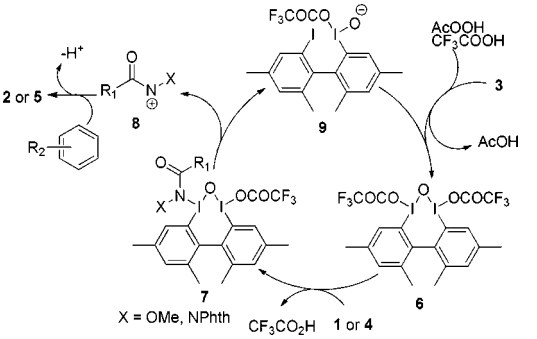
Scheme 2. Scope of Hydrazination of Arenes



Reaction conditions: **4** (1 equiv), arene (20 equiv), **3** (10 mol %), AcOOH (2.2 equiv), CF_3CO_2H (5 equiv), in DCE (0.2 M). Yields are given for isolated products after chromatography. The minor regioisomeric position is labeled with the respective carbon atom number. [a]Arenes used (2 equiv). [b]Ratio of regioisomeric products was measured by weight of individual isolated products. [c]Ratio of inseparable regioisomeric products measured by ^{1}H NMR of isolated products. [d]Arene used (5 equiv). [e]Reaction conditions: arene (1 equiv), **4** (3 equiv), **3** (10 mol %), AcOOH (2.2 equiv), CF_3CO_2H (5 equiv), in DCE (0.2 M).

conditions in good yields and exclusive regioselectivity (Scheme 2, products **5k**, **5l**). Polysubstituted arenes efficiently hydrazinated under the developed reaction conditions with high selectivity and good to excellent yields (Scheme 2, products **5m**–**5r**). To our delight, a variety of functional groups such as carboxylic acids, iodides, amides and ethers were tolerated. As an illustration of the synthetic versatility of the organocatalytic method, we next demonstrated hydrazination of functionalized biologically active probes. Using excess of reagent **4**, a hydrazinated analogue of vitamin P was obtained as single regioisomer with 92% yield (Scheme 2, product **5s**). A competitive hydrazination was observed in the case of ibuprofen analogue with satisfactory yield (Scheme 2, product **5t**). Future transformations of hydrazination products **5** are possible to various derivatives of anilines and arylhydrazines under mild reaction conditions (see the Supporting Information for details).

Scheme 3. Proposed Catalytic Cycle



There was no detection of *meta*-substituted products besides *ortho*- and *para*-isomers. Reaction rate is exceptionally faster for electron rich arenes compared to electron deficient arenes. A primary kinetic isotope effect is equal 1.0 and indicates that C–H bond cleavage does not occur as the rate-determining step of the reaction (see the Supporting Information for details). On the basis of these findings, mechanistically we assume that initially aryl iodide **3** is oxidized by peracetic acid to the active hypervalent *μ-oxo*-bridged **6**. The ligand substitution at iodine(III) by **1** or **4** generates species **7**, which undergoes oxidative fragmentation to form nitrenium ion **8** and active hypervalent species **9**, which further converted to **6** under the reaction conditions. Then the arene attacks the electron-deficient nitrenium ion **8** to provide the desired products **2** or **5**.

In conclusion, we developed a new highly efficient, mild, atom-economical, oxidative intermolecular process for the introduction of amine or hydrazine groups into nonpre-functionalized arenes. Intermolecular formations of C–N bonds occur in the presence of substoichiometric amounts of small organic molecules. The desired products of monoamination and hydrazination were selectively formed by the functionalization of arenes at ambient temperature. The developed method was utilized for arenes and for the late stage functionalization of biologically active molecules.

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Supporting Information Available. Experimental procedures, full characterization of new compounds, CIF file for compound **5s**, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.