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Intermolecular Oxidative C−N Bond Formation under Metal-Free Conditions: Control of Chemoselectivity between Aryl sp^2 and Benzylic sp^3 C−H Bond Imidation

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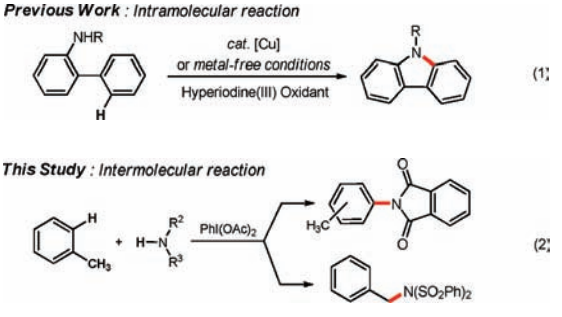
Supporting Information

ABSTRACT: A new synthetic approach toward intermolecular oxidative C−N bond formation of arenes has been developed under transition-metal-free conditions. Complete control of chemoselectivity between aryl sp^2 and benzylic sp^3 C−H bond imidation was achieved by the choice of nitrogen sources, representatively being phthalimide and dibenzenesulfonimide, respectively.

The importance of constructing C−N bonds of aromatic compounds has captured the attention of organic chemists over several decades since numerous pharmaceuticals, agrochemicals, polymers, and biologically relevant molecules incorporate the aryl nitrogen functionality.[1] This aspect has led to the development of a range of notable C−N cross-coupling reactions by employing preactivated starting materials, most representatively (hetero)aryl (pseudo)halides to react with amines or amides.[2] Of particular importance are the Buchwald−Hartwig type *N*-arylation procedures using palladium or copper catalysts with the aid of amine or phosphine ligands.[3]

Despite these significant advances, a direct C−N bond-forming reaction, particularly methods that enable the direct functionalization of C−H bonds of arenes, has been a focus of recent interests because of its straightforward and economical advantages over present procedures employing prefunctionalized substrates.[4−8]



Recently, we have been interested in the cross-coupling of aromatic C−H bonds with certain nitrogen nucleophiles to afford *N*-arylated compounds.[9] In this context, we developed an intramolecular oxidative C−N bond-forming reaction of 2-amidobiphenyls to afford carbazoles at ambient conditions (eq 1).[9d] It was significant to observe that the oxidative cyclization proceeded under either Cu-facilitated or metal-free conditions by the action of hypervalent iodine(III) species. Mechanistic studies indicated that catalytic amounts of copper species work as an activator of the employed iodine(III) oxidant, thus generating *N*-iodoamido or its radical cationic species as a key intermediate. Based on this study, we envisaged that *an intermolecular C−H/N−H cross-coupling of simple arenes* would be possible if suitable nitrogen sources were sought enabling similar intermediates to form (eq 2). Herein, we describe the realization of such an intermolecular C−H imidation of arenes using hypervalent iodine(III) as a single oxidant under transition-metal-free conditions. More significantly, *complete control of chemoselectivity in the imidation of aryl sp^2 and benzylic sp^3 C−H bond was achieved by the choice of suitable nitrogen sources.*

To test our hypothesis on the intermolecular *N*-arylation of simple arenes, succinimide (**2a**) was initially employed to react with benzene using $PhI(OAc)_2$ (IBDA) under various conditions (Table 1). Unlike the intramolecular case,[9d] no conversion was observed at temperatures below 80 °C using IBDA irrespective of the presence of copper additives (entries 1 and 2). Gratifyingly, however, the desired product (**3a**) started to form upon an increase in reaction temperature (entry 3), and a complete conversion was attained at 140 °C using 5 equiv of IBDA alone (entry 4).[10] The loading of reduced amounts of oxidant resulted in lower conversion (entry 5). On the other hand, other sources of hypervalent iodine(III) oxidants or single electron oxidants gave either poor or no conversion under otherwise identical conditions (entries 6−9).

With the newly developed protocol of intermolecular oxidative C−H imidation, a variety of imides were next subjected to the optimized conditions (Table 2). Six-membered imides such as glutarimide (entry 2) or its derivative (entry 3) were still facile reactants albeit with slightly lower efficiency when compared to five-membered succinimide. An excellent level of product yields was observed from the imidation of benzene with phthalimide derivatives (entries 4−7), even allowing the use of lower amounts of oxidant (entry 5). Electronic variation of the imide sources did not much influence the reaction efficiency although a nitro substituent slightly lowered the product yield (entry 7). 1,8-Naphthalimide underwent the C−H imidation reaction with similar efficiency (entry 8). It is noteworthy that mixed imides such as benzoic sulfimide (saccharin) also exhibited high reactivity (entry 9). However, amides rather than imides or sulfimides

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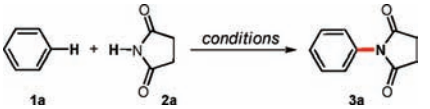
Table 1. Examination of Various Oxidant[a]



entry	oxidant	temp (°C)	conv (%)	yield (%)[b]
1	$PhI(OAc)_2$	80	<1	<1
2[c]	$PhI(OAc)_2$	80	<1	<1
3	$PhI(OAc)_2$	120	41	32
4	**$PhI(OAc)_2$**	**140**	**100**	**90 (86)**[d]
5[e]	$PhI(OAc)_2$	140	89	74
6	PhI(OH)(OTs)	140	5	3
7	$PhI(OTFA)_2$	140	<1	<1
8	*t*-BuOOBz	140	<1	<1
9	$K_2S_2O_8$	140	<1	<1

[a] Conditions: benzene (**1a**, 1.5 mL), succinimide (**2a**, 0.3 mmol), and oxidant (5 equiv) were added into a screw-capped vial and reacted for 4 h at the indicated temperature. [b] NMR yield. [c] $Cu(OTf)_2$ (5 mol %) was added. [d] Isolated yield in parentheses. [e] 3 equiv of $PhI(OAc)_2$ were used.

offered poor reaction efficiency. For instance, amidation of benzene with 2-oxazolidone resulted in a low yield (entry 10).

The optimized imidation procedure was subsequently applied to a range of simple arenes using phthalimide (**2d**) *as a cheap and readily detachable nitrogen source* (Table 3). All reactions were carried out at 140 °C for 4 h by employing 3 equiv of $PhI(OAc)_2$. *p*-Xylene was efficiently monoimidated (entry 1) while the reaction of 1,4-difluorobenzene occurred with a rather lower yield (entry 2). Although the present imidation protocol was highly facile leading to satisfactory chemical yields in most cases, it did not display a high level of regioselectivity in the case of substituted arenes. For instance, reaction of *o*-xylene furnished an equal ratio of two possible regioisomers (entry 3). The regioselectivity was a bit increased in the imidation of 1,2-dichlorobenzene, slightly favoring the remote position to the existing substituents (entry 4).

A similar trend of site selectivity was observed in the oxidative imidation of 1,2,3-trisubstituted arenes. However, in this case, imidation takes place more favorably at the *ortho*-position to the existing substituents (entries 5−7). Importantly, a sterically congested 1,3,5-trisubstituted arene also participated in the cross-coupling process with high efficiency (entry 8). For monosubstituted arenes, imidation smoothly took place to afford desired products in excellent yields, but as a mixture of *ortho*-, *meta*-, and *para*-regioisomers (entries 9−11). *It is notable that the imidation could be carried out using only 3 equiv of arenes in 1,2-dichloroethane solvent with similar efficiency, thus widening the synthetic utility of this methodology* (entries 7, 8, and 12).

During the course of our studies on the sp^2 aryl C−N bond formation, it was found that the benzylic sp^3 C−H bond could also be imidated by the choice of suitable nitrogen sources.[11,12] Among the various imides and derivatives screened, sulfonyl-containing imides such as dibenzenesulfonimide or saccharin turned out to be effective for this conversion under otherwise identical conditions (Table 4). Toluene was readily converted to its imido product (**5a**) in satisfactory yield at 120 °C using 4 equiv of $PhI(OAc)_2$. The benzylic imidation was also highly selective to afford only monoimides as demonstrated in the

Table 2. Oxidative Amination with Various Nitrogen Sources[a]

entry	amide	product		yield (%)[b]
1	(**2a**)	(**3a**)		86
2	(**2b-c**)		R = H (**3b**)	56
3			R = Me (**3c**)	67
4	(**2d-f**)		R = H (**3d**)	96
5[c]			R = H (**3d**)	80
6			R = Me (**3e**)	99
7			R = NO_2 (**3f**)	87
8	(**2g**)	(**3g**)		87
9	(**2h**)	(**3h**)		90
10	(**2i**)	(**3i**)		28

[a] Conditions: benzene (**1a**, 1.5 mL), imide (**2**, 0.3 mmol), and PhI-$(OAc)_2$ (5 equiv) were added into a screw-capped vial and reacted for 4 h at 140 °C. [b] Isolated yield. [c] $PhI(OAc)_2$ (3.0 equiv) was used.

reaction of *p*- and *o*-xylene (**5b** and **5d**, respectively). Intriguingly, saccharin also exclusively underwent the benzylic sp^3 C−H imidation albeit with moderate efficiency (e.g., **5e**) while its imidation at the aryl sp^2 C−H bond took place at 140 °C in excellent yield (Table 2, entry 9).[13]

It has to be addressed that the benzylic imidation was almost exclusive with no accompanying aryl sp^2 C−H imidation under the employed conditions when dibenzenesulfonimide or saccharin was employed as a nitrogen source. In fact, when a competition experiment was performed between benzene and *p*-xylene using saccharin, the benzylic position was observed to be imidated much faster than the aryl imidation, thus explaining the complete chemoselectivity switch.[12] *This result is highly significant in that chemoselective imidation is exclusively achieved with the same substrates simply by the choice of imide sources.*

In order to elucidate the present C−H imidation mechanism, a series of experiments were subsequently performed with the following results:[12] (i) no kinetic isotope effect ($k_{H/D}$ = 1.0) was observed in the sp^2 aryl C−N bond formation, (ii) a competition experiment employing an equimolar amount of benzenes bearing 1,2-dimethyl (**1d**) and 1,2-dicholoro (**1e**) substituents revealed that **1d** underwent the reaction 13 times faster than **1e**, and (iii) *in situ* high resolution ESI mass analysis of the reaction mixture containing mesitylene, phthalimide, and $PhI(OAc)_2$ showed peaks at m/z = 349.9675 and 431.9699, which were assigned to be $[NPhth(IPh)^+]$ and $[NPhth\{I(OAc)Ph\}-Na^+]$, respectively.

Based on these observations, an electrophilic aromatic substitution pathway is proposed in the aryl sp^2 C−H bond imidation (Scheme 1 using phthalimide as a model reagent). It is postulated

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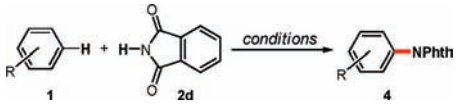
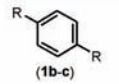
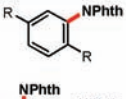
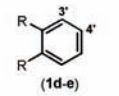
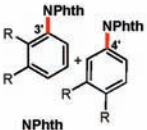
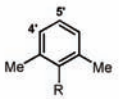
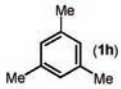
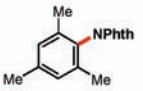
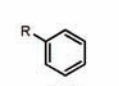
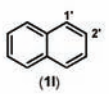
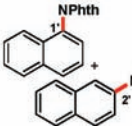
Table 3. Oxidative Imidation of Arenes with Phthalimide[a]



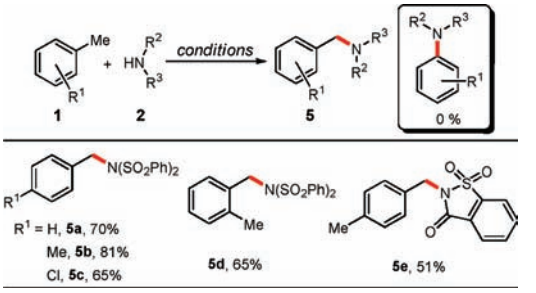
entry	arene	product		yield(%)[b,c]
1	 (1b-c)		R = Me (4b)	81
2			R = F (4c)	38
3	 (1d-e)		R = Me (4d)	72 (3' : 4' = 1 : 1)
4			R = Cl (4e)	79 (3' : 4' = 2 : 3)
5	 (1f-g)		R = OMe (4f)	40 (4' : 5' = 1.3 : 1)
6			R = Cl (4g)	74 (4' : 5' = 2.2 : 1)
7			R = Cl (4g)	73[d] (4' : 5' = 2.7 : 1)
8	 (1h)		(4h)	80 (79[d])
9	 (1i-k)		R = Me (4i)	99 (o- : m- : p- = 1.7 : 1 : 1.1)
10			R = Cl (4j)	80 (o- : m- : p- = 1.4 : 1.1 : 1)
11			R = OAc (4k)	99 (o- : m- : p- = 1.2 : 1 : 1.1)
12	 (1l)		(4l)	68[d] (1' : 2' = 1 : 1)

[a] Conditions: arene (**1**, 1.0 mL), phthalimide (**2c**, 0.3 mmol), and $PhI(OAc)_2$ (3 equiv) were added into a screw-capped vial and reacted for 4 h at 140 °C. [b] Overall isolated yield. [c] Ratio of isomeric mixtures was determined by ^1H NMR. [d] 3 equiv of arene were used in $ClCH_2CH_2Cl$ solvent at 140 °C for 4 h.

that the treatment of **2d** with $PhI(OAc)_2$ would furnish a *N*-(phenylacetoxyiodo)imido species **6**. In fact, there were precedent examples reporting the formation of *N*-iodo(III)-amino complexes from the reaction of a hyperiodine(III) oxidant with imidazole.[14,15] It is assumed that an electrophilic attack of arene at the iodoimido species **6** affords the C−H imidated product upon release of acetic acid and iodobenzene.

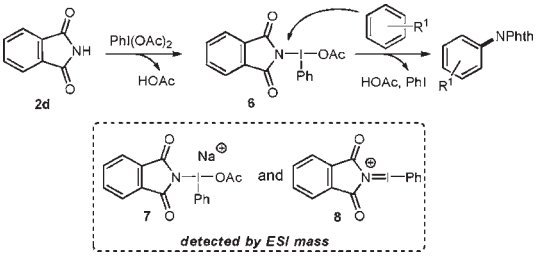
Although a single electron transfer (SET) pathway cannot be ruled out,[16] this alternative is believed to be less likely because aromatic radical cations are known to be induced only when electron-rich arenes such as *p*-substituted phenol ethers or thiophenes were employed at low temperatures (−78∼25 °C). However, in our case, electron-deficient arenes were also viable substrates for the imidation under the developed conditions (e.g., Table 3, entries 2, 4, 6, and 10). While the reason for low regioselectivity observed in the imidation of substituted benzenes is not clearly described at the present stage, it might be ascribed to the high reaction temperature employed. Nevertheless, our result is still intriguing because the observed selectivity trend is in contrast to the recently developed metal-catalyzed Friedel−Crafts type C−C bond formation which is inherently sensitive to electronic factors.[17,18]

Table 4. Oxidative Imidation of Benzylic C−H Bond[a,b]

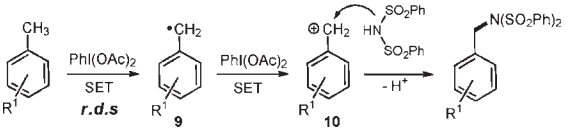


[a] Conditions: arene (**1**, 1.0 mL), imide (2, 0.3 mmol), and $PhI(OAc)_2$ (4.0 equiv) were added into a screw-capped vial and reacted for 4 h at 120 °C. [b] Isolated yield.

Scheme 1. Proposed Path of Oxidative Arene Imidation



Scheme 2. Proposed Path of Oxidative Benzylic Imidation



In contrast to the sp^2 aryl C−N bond formation, oxidative benzylic imidation displayed significant kinetic isotope effects ($k_{H/D}$ = 2.6), implying that benzylic sp^3 hydrogen abstraction in this case might be involved in the rate-limiting step (Scheme 2). A kinetic profile study revealed that the reaction rate was almost independent with regard to dibenzenesulfonimide concentrations under the employed conditions.[12] In addition, when benzylacetate was subjected to the reaction conditions, no imidated product was observed to suggest that the reaction does not proceed via an acetate intermediate. These results led us to propose that a single electron transfer oxidation pathway might be engaged in the generation of a benzyl radical **9**, which is further oxidized to a cationic species **10**, and then subsequent nucleophilic attack of dibenzenesulfonimide provides products, being imidated at the benzylic site. We believe that the origin of this site selectivity might be attributed to the difference in the electronic nature between the nitrogen sources employed.[19] It can be assumed that dibenzenesulfonimide has a lower reactivity toward the $PhI(OAc)_2$ oxidant, thus disfavoring the above proposed electrophilic aromatic substitution pathway of sp^2 aryl imidation as depicted in Scheme 1.

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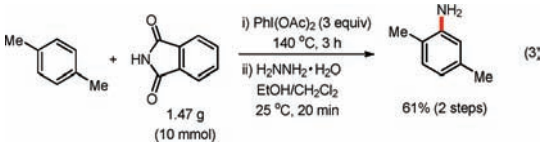
With the developed protocol in hand, we next demonstrated its synthetic utility in the preparation of 2,5-dimethylaniline (eq 3). A gram scale imidation of *p*-xylene was easily performed under the optimized conditions, and *in situ* hydrazinolysis of formed *N*-arylphthalimide was followed to furnish the desired product in 61% yields over two steps.



In conclusion, we have developed a highly efficient intermolecular oxidative C−H imidation of arenes with (sulf)imides using $PhI(OAc)_2$ as an oxidant under metal-free conditions.[20] More significantly, complete control of chemoselectivity was achieved in the imidation between aryl sp^2 and benzylic sp^3 C−H bonds simply by the choice of nitrogen sources, representatively being phthalimide and dibenzenesulfonimide, respectively. Although detailed mechanistic descriptions and the development of milder reaction conditions are still desired, it is believed that this new protocol will open a new avenue for the forthcoming more practical and selective C−N bond construction from unactivated C−H bonds.

■ ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and characterization of new compounds, including ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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