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Iron(II) Bromide-Catalyzed Intramolecular C−H Bond Amination [1,2]-Shift Tandem Reactions of Aryl Azides

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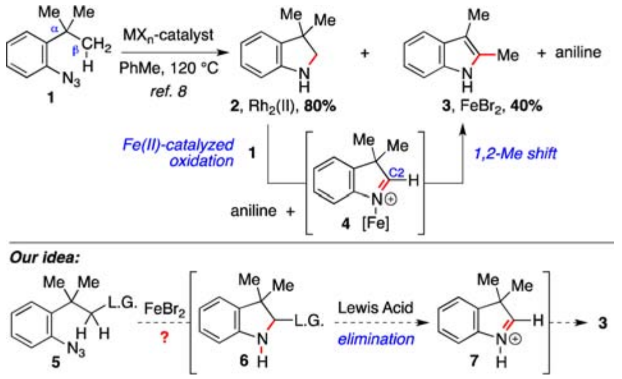
S Supporting Information

ABSTRACT: Iron(II) bromide catalyzes the transformation of *ortho*-substituted aryl azides into 2,3-disubstituted indoles through a tandem ethereal C−H bond amination [1,2]-shift reaction. The preference for the 1,2-shift component of the tandem reaction was established to be Me < 1° < 2° < Ph.

The ability of tandem reactions to rapidly increase the molecular complexity of simple substrates continues to inspire the efforts of synthetic groups to incorporate new reactions into these cascades.[1,2] While transition-metal-catalyzed C−H bond amination is emerging as a useful synthetic process,[3−5] this reaction has never been harnessed to initiate a cascade reaction. Further, the incorporation of migratorial processes into these cascade sequences remains rare despite the potential of these processes to transform simple substrates into complex, functionalized products.[6] We have demonstrated that metal nitrenes originating from *ortho*-alkenyl-substituted aryl azides can engage in cascade reactions where electrocyclization of the rhodium nitrene triggers a subsequent, selective 1,2-shift.[7] Initiating these tandem reactions with a C−H bond amination reaction—ideally using an inexpensive, nontoxic first-row transition-metal catalyst—would be highly appealing, as it would minimize the amount of functionality required in the starting material. Towards this goal, we report our development of an iron(II) bromide-catalyzed ethereal C−H bond amination 1,2-migration tandem reaction that efficiently and selectively transforms *ortho*-substituted aryl azides into 2,3-disubstituted indoles.

An unexpected observation during our optimization study into the formation of indoline **2** from aryl azide **1** prompted our interest in using an amination reaction to initiate a tandem reaction sequence (Scheme 1). A screen of transition-metal complexes identified $Rh_2(esp)_2$ to be the most efficient catalyst for the intramolecular C−H bond amination of **1**, which provided indoline **2**.[8] This screen also revealed that $FeBr_2$ decomposed the aryl azide. The expected indoline, however, was not observed. Instead, a mixture of 2,3-dimethylindole **3** and aniline were formed. We attributed the formation of these products to an Fe-mediated oxidation of indoline **2**,[9] which would produce iminium ion **4** and aniline if the aryl azide was the oxidant.[10] A 1,2-methyl shift from **4** would then produce the observed indole. We anticipated that this tandem amination−migration process might be rendered a viable synthetic method if the mechanism for iminium ion formation were changed from an oxidative process (requiring a stoichiometric oxidant, azide) to an elimination step. We envisioned that this modification could be achieved if one of the *β*-hydrogen atoms in **1** was replaced with a leaving group. Transition-metal-catalyzed C−H bond amination of **5** would form indoline **6**, which could undergo Lewis acid-catalyzed elimination of the leaving group to form iminium ion **7** and trigger the desired 1,2-migratorial process.[11]

Scheme 1. Observation of a Fe(II)-Promoted Tandem Reaction



Our pursuit of triggering a tandem C−H bond amination−elimination−migration sequence started by investigating the reactivity of aryl azides **8** toward transition-metal complexes (Table 1). We began by substituting the *β*-hydrogen atom in **1** with an alkoxy group and examining the reactivity of the resulting azides toward iron(II) bromide.[11−13] While the use of an acetate lead only to aniline formation (entry 1), changing R to Et led to nearly complete 2,3-dimethylindole formation (entry 2). The reaction conversion was dependent on both the temperature as well as catalyst loading with severe attenuation of indole formation observed when either was reduced (entries 2−4).

Upon completion of our initial optimization studies using iron(II) bromide, other transition-metal complexes were examined to determine if they could catalyze this tandem reaction (Table 1). Despite their proven ability to catalyze N-atom transfer reactions from azides, our survey of Rh_2(II),[14] Ir(I),[15] Co(I),[16] Ru(III),[17] or Cu(I) complexes[18] did not identify any competent catalyst for our process (entries 5−8). The reaction also proved sensitive to the Lewis acidity of the iron salt:[19] no reaction was observed if the counterion or the oxidation state was changed (entries 9−11). From our studies, iron(II) bromide appears unique in its ability to catalyze the C−H bond amination reaction, the elimination, and the 1,2-methyl shift

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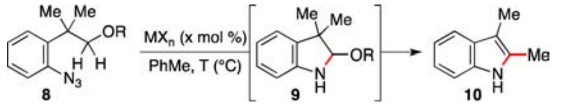
Table 1. Development of Optimal Conditions



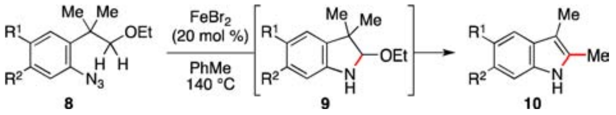
entry	catalyst[b]	mol %	R	temp	yield, %[a]
1	$FeBr_2$	20	Ac	120	10[c]
2	$FeBr_2$	20	Et	120	75
3	$FeBr_2$	10	Et	120	16
4	$FeBr_2$	20	Et	140	85
5	$Rh_2(esp)_2$	20	Et	120	0
6	CoTTP	20	Et	120	0
7	$RuCl_3 \cdot nH_2O$	20	Et	120	0
8	CuI	20	Et	120	0
9	ZnI_2	20	Et	120	trace
10	$FeCl_2$	20	Et	120	0
11	$FeBr_3$	20	Et	120	20

[a] As determined using ^{1}H NMR spectroscopy and CH_2Br_2 as the internal standard. [b] No desired product was observed in transition-metal catalyst absence; only azide decomposition was obtained. [c] Aniline formed.

with the optimal conditions to be 20 mol % catalyst loading in toluene at 140 °C.

With optimal conditions, the scope of our iron(II) bromide-catalyzed tandem C−H bond amination−elimination 1,2-methyl migration reaction was investigated (Table 2). We found that the reaction yield was not affected by the electronic nature of the aryl azide with consistent yields of the 2,3-dimethylindole obtained for both electron-releasing and -withdrawing groups. Despite the established reactivity of olefins with iron nitrenes,[9c] we found that aryl azide **8e** bearing a styryl group was transformed into the indole product, albeit with a diminished yield (entry 5). Our reaction enables the synthesis of 6-substituted indoles (e.g., **10g**), which cannot be made regioselectively using the Fischer indole reaction.[20] These results indicate that changing the electronic nature of the aryl azide is not detrimental to the outcome of our tandem reaction.

Table 2. Scope of Fe(II)-Catalyzed Tandem Reaction

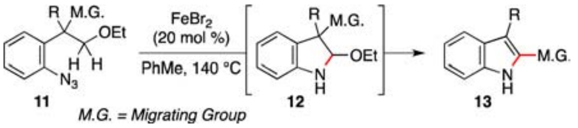


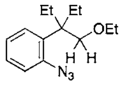
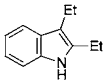
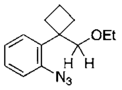
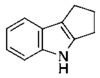
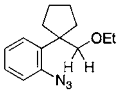
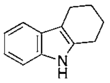
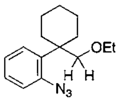
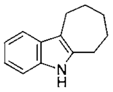
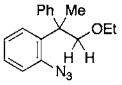
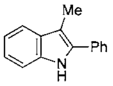
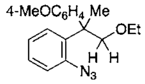
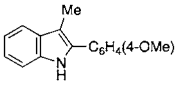
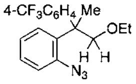
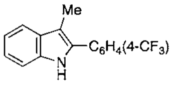
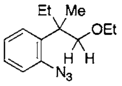
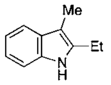
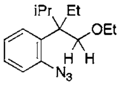
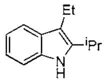
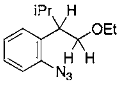
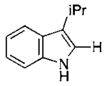
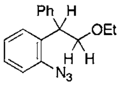
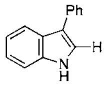
entry	no.	R^1	R^2	yield, %[a]
1	a	H	H	85
2	b	OMe	H	70
3	c	Me	H	98
4	d	Ph	H	85
5	e	PhCH=CH	H	50
6	f	Br	H	81
7	g	H	Br	79

[a] Isolated after silica gel chromatography.

Next, the effect of changing the identity of the migrating group on the Fe(II)-catalyzed C−H bond amination 1,2-migration reaction was investigated (Table 3). We found that our reaction was not limited to 1,2-methyl shifts, but that ethyl group migrations as well as ring expansions could be triggered (entries 1−4). For the latter, the reaction was not constrained by the alleviation of ring strain: The highest reaction yield was obtained from the expansion the cyclohexyl substituted aryl azide **11d** in comparison to cyclobutyl and cyclopentyl substrates (entries 2−4).

Table 3. Effect of Changing the Migrating Group Identity on the Tandem Reaction



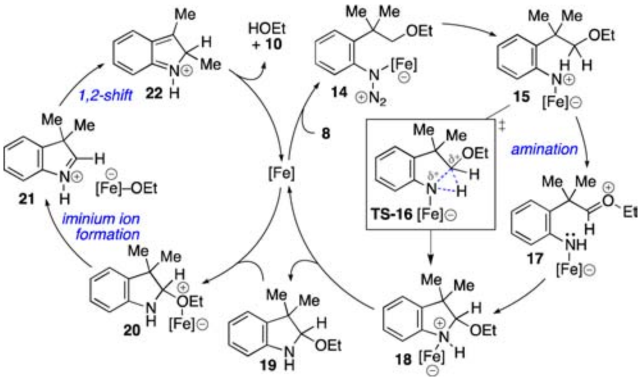
entry	#	aryl azide	indole	yield, %[a]
1	a			83
2	b			65[b]
3	c			69
4	d			78
5	e			95
6	f			58
7	g			dec
8	h			83
9	i			60[b]
10	j			50
11	k			42[c]

[a] Isolated after silica gel chromatography. [b] Aniline obtained as a byproduct. [c] Determined using ^{1}H NMR spectroscopy with CH_2Br_2 as internal standard.

Next, we determined if any selectivity could be observed during the migration component of the tandem reaction. We began by examining aryl azides that contained both methyl and aryl groups (Table 3, entries 5−7). To our delight, we found that submission of these substrates to reaction conditions resulted in exclusive aryl group migration to afford 2-aryl-3-methylindoles, presumably via a phenonium ion. This reaction, however, was dependent on the electronic nature of the aryl group with only decomposition observed for azide **11g** bearing an electron-deficient arene. With successful differentiation between sp^2 and sp^3 carbons, we were curious if our reaction could distinguish between different sp^3-substituted migrating carbons (entries 8 and 9). To examine this, we submitted aryl azide **11h** to reaction conditions. To our surprise, we found that only ethyl group migration occurred to provide 2-ethyl-3-methylindole as the solitary product. To determine if this high selectivity was general, azide **11i** bearing both isopropyl and ethyl groups was submitted to reaction conditions, affording 2-isopropyl-3-ethylindole as the only product (entry 9). Finally, to test for alkyl or aryl group migration in the presence of an α-hydrogen azides, **11j** and **11k** were examined (entries 10 and 11). While diminished yields were obtained, only 3 substituted indoles **11j** and **11k** were observed from these azides, revealing that these groups do not migrate when a hydrogen is present.[21] From these results, a preliminary migratorial aptitude scale of our reaction can be established to be: Me < 1° < 2° < Ph.

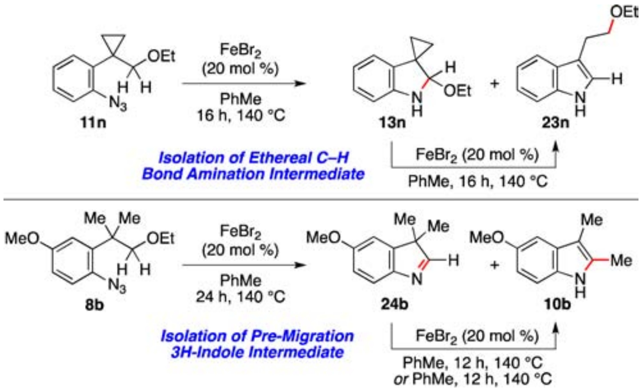
While a number of mechanisms can explain our transformation,[21] we interpret our results to indicate that iron(II) bromide functions as both an N-atom transfer catalyst and a Lewis acid (Scheme 2). Coordination of the iron catalyst to the aryl azide (to form **14**)[23] triggers the extrusion of N_2 to form iron nitrene **15**.[24] While the ethereal C−H bond amination reaction could be concerted (via **TS-16**),[11a] a stepwise process is also possible: hydride transfer from **15** forms oxocarbenium ion **17** that is attacked by the proximal amine to form indoline **18**.[25] Coordination of the Lewis acidic iron salt to the ethyl ether promotes the generation of iminium ion **21**, which triggers the 1,2-shift.[26] Subsequent deprotonation of **22** by iron ethoxide completes the catalytic cycle.

Scheme 2. Possible Mechanisms for Fe-Catalyzed Tandem Reaction

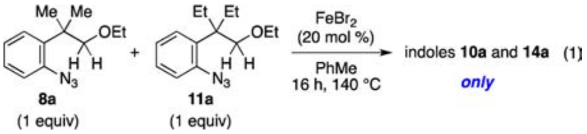


In our optimization studies, we isolated two potential heterocyclic intermediates, whose reactivity toward the reaction conditions support our proposed mechanism (Scheme 3). When cyclopropyl-substituted aryl azide **11n** was exposed to iron(II) bromide, a mixture of indoline **13n** and indole **23n** was isolated. Isolation of indoline **13n** provides support that C−N bond formation occurs through an ethereal C−H bond amination reaction. The lack of fragmentation of the cyclopropane suggests that this amination reaction does not proceed through an H-atom abstraction−radical recombination reaction.[22e,h,27] Resubmission of **13n** to reaction conditions produced indole **23n**; in the absence of iron(II) bromide no reaction was observed. The reactivity of methoxy-substituted **8b** was also consistent with our mechanistic hypothesis. The isolation of 3*H*-indole **24b** indicates that the 1,2-methyl shift occurs after elimination of the ethoxide group. In contrast to **13n**, thermolysis of **24b** forms the 2,3-dimethylindole product in the absence of the Lewis acid. Together these results suggest that iron(II) bromide is required for both C−H bond amination as well as iminium ion formation but not for 1,2-alkyl migration.

Scheme 3. Isolation of Reactive Intermediates



To probe the 1,2-shift reaction mechanism, a double crossover experiment was performed (eq 1). Exposure of a 1:1 mixture of **8a** and **11a** to reaction conditions resulted in the formation of only two indoles. The lack of crossover products suggests that the 1,2-shift component of our tandem reaction is a concerted process, or if stepwise, the shift occurs faster than diffusion of the migrating group.



In conclusion, we have discovered that iron(II) bromide promotes tandem C−H bond amination 1,2 migration reactions of *ortho*-substituted aryl azides to enable the formation of 2,3-disubstituted indoles. The 1,2-shift component of our tandem reaction is remarkably selective, and our results enable prediction of the migration aptitude to be Me < 1° < 2° < Ph. Our future studies are aimed at achieving a better understanding of the mechanism of our tandem reaction as well as further exploring iron-catalyzed C−H bond amination reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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