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Denitrogenative Imidoyl Radical Cyclization: Synthesis of 2-Substituted Benzoimidazoles from 1-Azido-2-isocyanoarenes

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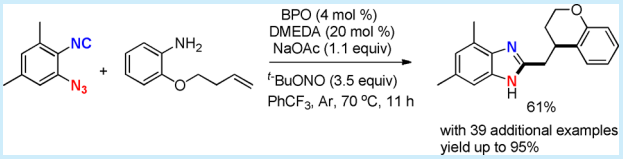
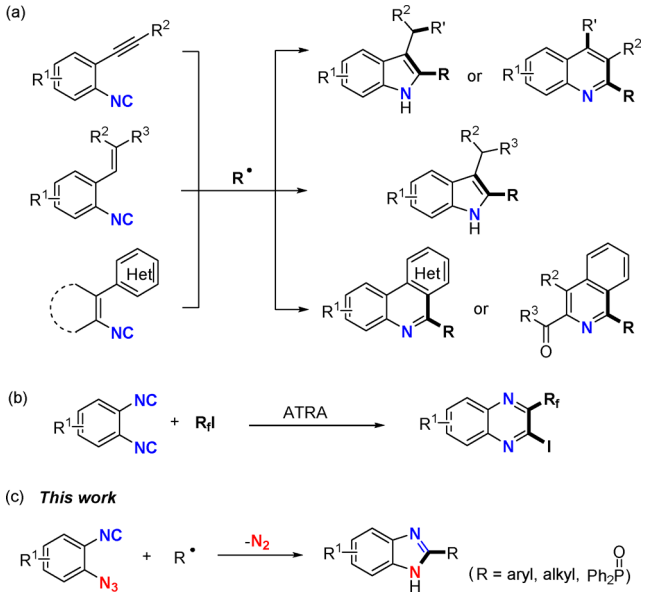
Supporting Information

ABSTRACT: A novel access to 2-substituted benzoimidazoles, through unprecedented denitrogenative imidoyl radical cyclization of 1-azido-2-isocyanoarenes, has been developed. This tandem radical process was initiated by adding a C- or P-centered radical to isocyanide, followed by cycloaddition of the imidoyl radical to the azido group. Then, nitrogen loss and hydrogen abstraction of the resulting aminyl radical from surroundings delivered 2-substituted benzoimidazoles. Carbon radicals generated from another annulation process could also be applied, furnishing various heterocycle linked benzoimidazole derivatives.



Isocyanide has been extensively studied in acid-promoted multiple component reactions (MCRs)[1] and transition-metal-catalyzed insertion processes due to its unique structure and reactivity.[2] It can also react with various carbon- or heteroatom-centered radical species to generate imidoyl radical intermediates for further transformations.[3] Synthetic application of an imidoyl radical mainly focuses on N-heterocycle synthesis through its addition to intramolecular alkyne,[4] alkene,[5] or arene[6] functionalities, generating various substituted indole, quinoline, isoquinoline, and phenanthridine derivatives (Scheme 1a). For example, 2-isocyanobiphenyls were studied in depth with various radical sources to give C6 diversified phenanthridines through intramolecular homolytic aromatic substitution (HAS) of an imidoyl radical intermediate.[6] Recently, Studer and Yu independently demonstrated a cascade radical cycloaddition of *ortho*-diisocyanoarenes to give iodoquinoxalines through an atom transfer radical addition (ATRA) process, in which one of the isocyano carbons acted as the imidoyl radical acceptor (Scheme 1b).[7] However, cycloaddition of an imidoyl radical to a heteroatom by forming a C−heteroatom bond is unprecedented.

Scheme 1. Imidoyl Radical Cyclization Reactions



In continuation of our interest in heterocycle synthesis using isocyanides,[8] we recently demonstrated that 1-azido-2-isocyanoarenes[9] could be used as a new class of functionalized isocyanide for the synthesis 1,2,3-triazolo[1,5-*a*]quinoxalines through copper-catalyzed azide−alkyne [3 + 2] cycloaddition (CuAAC) followed by isocyanide insertion.[10] Meanwhile, organo azide is widely used in C−N bond formation through transition-metal-catalyzed or photoinduced azide decomposition and active nitrenoid or nitrene formation.[11] However, reactions through addition of carbon radical to azide, forming an aminyl radical after nitrogen loss, are less common.[12] An early work by Montevecchi demonstrated that cyclization of a vinyl radical, generated by addition of benzenesulfanyl radical to the triple bond of 2-azidodiphenylacetylene, onto an aromatic azide followed by denitrogenation and hydrogen abstraction could give the corresponding indole derivatives.[12a] Inspired by these studies,[12] we speculate that denitrogenative imidoyl radical cyclization could be realized using 1-azido-2-isocyanoarenes as both imidoyl radical precursor and acceptor, to provide an alternative pathway to construct the benzoimidazole scaffold (Scheme 1c). It is reasonable to expect that heteroatom-centered radicals as well as carbon radicals which are generated from another annulation process could also be applied to this strategy. Thus, substituents at the C2 position of benzoimidazoles could be greatly diversified starting from the common 1-azido-2-isocyanoarene substrates.

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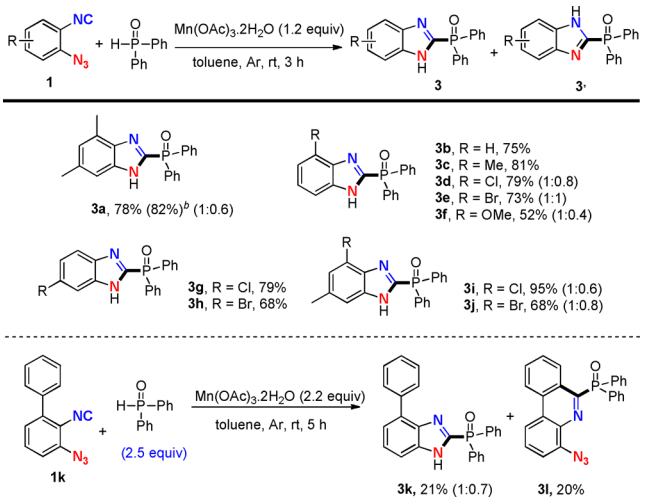
Phosphorus-containing compounds are applied widely in organic synthesis, pharmaceuticals, and material science.[13] Therefore, continuous interests have been paid in developing new C−P bond-forming methods,[14] including phosphinoyl radical-initiated imidoyl radical formation in the synthesis of 6-phosphorylated phenanthridines.[6q−v] We initiated the study with diphenylphosphine oxide as the radical precursor in a reaction with 1-azido-2-isocyano-3,5-dimethylbenzene **1a** to optimize the reaction conditions. It was found that $Mn(OAc)_3{\cdot}2H_2O$ could promote the reaction very well in toluene at room temperature for 3 h, and the products were isolated as a mixture of isomers **3a** and **3a′**, in a ratio of 1:0.6 in 78% yield (Scheme 2, and see

Scheme 2. Phosphinoyl Radical Initiated Cyclization[a]

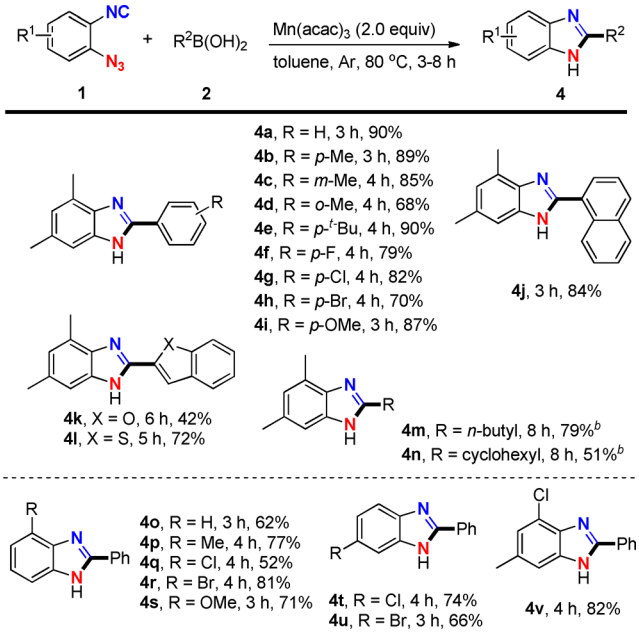


[a]Reaction conditions: **1** (0.10 mmol, 1.0 equiv), diphenylphosphine oxide (0.15 mmol, 1.5 equiv), $Mn(OAc)_3{\cdot}2H_2O$ (0.12 mmol, 1.2 equiv) in toluene (1.5 mL), rt for 3 h, in Ar. [b]1.0 mmol of **1a**, 5 h.

Supporting Information (SI) for details). Then, the generality of the current process was studied with a range of 1-azido-2-isocyanoarenes **1** with diphenylphosphine oxide. As shown in Scheme 2, 1-azido-2-isocyanoarenes bearing various substituents, such as Me, OMe, Cl, and Br at different positions, underwent the annulation smoothly to give the corresponding products **3a**−**3j** in 52−95% yields. In some cases, the products existed in equilibrium between the isomeric forms ranging from 1:1 to 1:0.4 as determined by ^{1}H NMR. While in the case of **3c**, **3g**, and **3h**, only one set of peaks for one of the isomers were seen. When 3-azido-2-isocyano-1,1′-biphenyl **1k**, which contained a competing benzene ring on the other side of the isocyano group, was tested under slightly modified conditions, benzoimidazole products **3k** and a phenanthridine derivative **3l** were isolated in 21% and 20% yield, respectively. The result suggested that the imidoyl radical intermediate cyclized almost equally fast on the azido group as compared with the benzene ring.

Next, the feasibility of using carbon radicals in the current denitrogenative cyclization reaction was investigated. A seminal work by Tobisu and Chatani in 2012 demonstrated that organoboron reagents could serve as radical precursors in reactions with 2-isocyanobiphenyls to give C6 aryl, heteroaryl, and alkyl substituted phenanthridines.[6a] Therefore, similar conditions were applied to 1-azido-2-isocyanoarene substrates **1** (Scheme 3). To our delight, 4,6-dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole **4a** was obtained in excellent yield (90%) from **1a** and phenyl boronic acid in the presence of $Mn(acac)_3$

Scheme 3. Organoboron Reagents Initiated Cyclization[a]



[a]Reaction conditions: **1** (0.10 mmol, 1.0 equiv), **2** (0.15 mmol, 1.5 equiv), $Mn(acac)_3$ (0.20 mmol, 2.0 equiv) in toluene (1.5 mL), 80 °C, 3−8 h, in Ar. [b]$Mn(acac)_3$ (0.30 mmol, 3.0 equiv), boronic acids **2** (0.30 mmol, 3.0 equiv).

(2.0 equiv) in toluene at 80 °C for 3 h (see SI for details). A variety of substituted phenyl boronic acids were also tolerable under the optimal reaction conditions, furnishing the corresponding C2 arylated benzoimidazoles **4b**−**4j** in 68−90% yields (Scheme 3). Importantly, heteroaryl as well as alkyl boronic acids could also be applied to the reaction (**4k**−**4n**), which greatly expanded the practicability of the method. 1-Azido-2-isocyanoarenes bearing various substituents, such as Me, OMe, Cl and Br, also underwent the reactions smoothly to give the corresponding products **4o**−**4v** in moderate to good yields.

Diazonium salts, preformed or generated in situ from anilines, have also been studied frequently as precursors of aryl radicals.[8e,15] When anilines bearing an appropriate alkenyl or alkynyl moiety at the *ortho* position are used, intramolecular aryl radical cyclization to the C−C unsaturated bond may occur prior to its addition to isocyanide. If alkyl or alkenyl radicals thus formed can participate in the current imidoyl radical cyclization, formation of more complicated benzoimidazoles derivatives is certainly expected. To test the hypothesis, 2-styrylaniline **5a** was initially tested (entry 1, Table 1). The direct arylation product **6a** was isolated in 65% yield, in which the alkenyl group remained unchanged due to its unfavorable position for cyclization. To our delight, the desired radical clock triggered cyclization indeed took place when relocating the C−C double bond two more atoms away from the anilinic ring. In the case of 2-(allyloxy)-aniline **5b**, sequential aryl radical cyclization to alkene, intermolecular imidoyl radical formation, and denitrogenative cyclization took place to deliver a novel bisheterocyclic system containing both dihydrobenzofurane and benzoimidazole scaffolds in one step in 57% yield (entry 2). By changing the linkage from oxygen to sulfur, and protected nitrogen in alkenyl anilines **5c**−**5d**, the corresponding dihyrobenzothiophene and indoline containing benzoimidazole derivatives **6c** and **6d** were obtained in 51% and 56% yield, respectively. 6-*Exo*-*trig* and 5-

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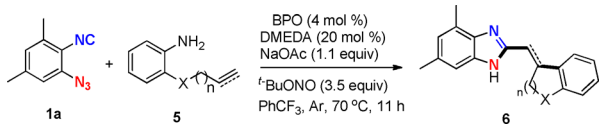
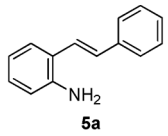
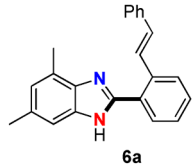
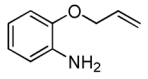
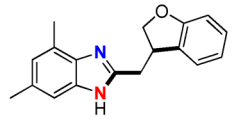
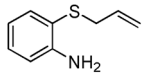
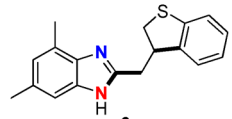
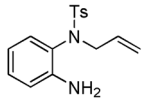
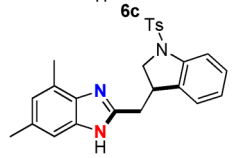
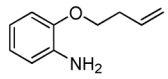
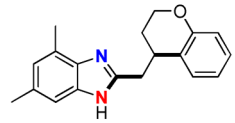
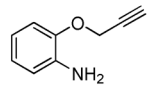
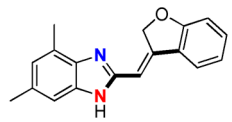
Table 1. Aniline Initiated Tandem Cyclization[a]

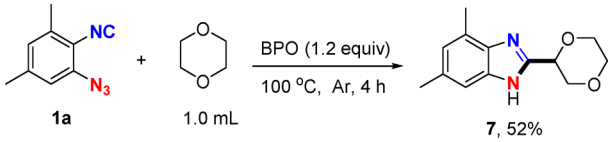


entry	aniline	product	yield (%)[b]
1	 5a	 6a	65
2	 5b	 6b	57
3	 5c	 6c	51
4	 5d	 6d	56
5	 5e	 6e	61
6	 5f	 6f	36

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **5** (0.30 mmol, 3.0 equiv) in $PhCF_3$ (1.5 mL), rt for 30 min, then 70 °C for 11 h, in Ar. [b]Isolated yield. BPO = benzoic peroxyanhydride.

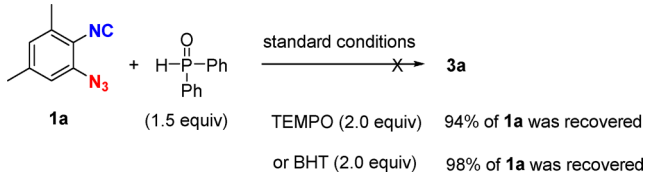
exo-dig radical cyclization were also feasible for substrates **5e** and **5f**, giving unique structures of **6e** and **6f** in moderate yields. In these processes, multiple chemical bonds including two C−C and one C−N bonds were formed consecutively in one step. A one-pot method for the synthesis of these bisheterocyclic products is not available in the literature. Moreover, these results provided solid evidence that radical intermediates were involved in the transformation.[8e,15c]

It is valuable that other radical species which is not accessible by the aforementioned approaches could also be applied to this method. For example, a 1,4-dioxanyl radical generated by heating BPO in 1,4-dioxane could also react with **1a** to afford the corresponding product **7** in 52% yield.[6c]



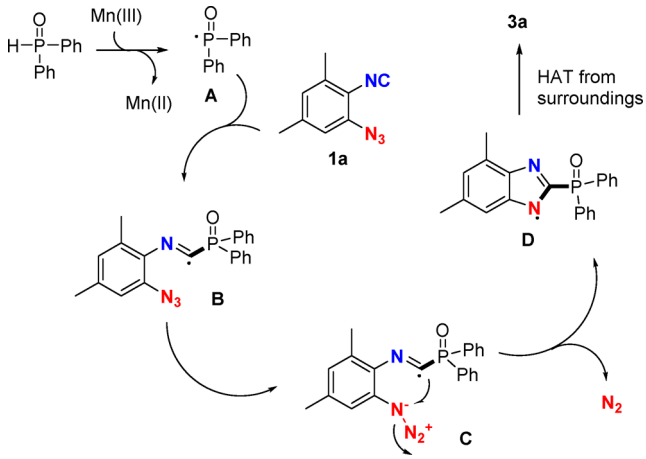
To further confirm the radical mechanism of the reaction, control experiments in the presence of radical scavengers including 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT) were performed (Scheme 4). The phosphorylation reactions were completely inhibited with most of **1a** recovered, indicating that radical intermediates were involved in the reaction.[6q−v]

Scheme 4. Radical Inhibiting Experiments



Based on the observations, a plausible mechanism for the formation of **3a** is proposed in Scheme 5. Initially, phosphorus

Scheme 5. Proposed Mechanism



radical **A** is formed in the presence of Mn(III) salts, which is a well-documented process.[6r,s] Then, addition of intermediate **A** to the terminal carbon of isocyanide **1a** generates the corresponding imidoyl radical **B**.[3] Subsequently, cycloaddition of the imidoyl radical to the azido group generated cyclized aminyl radical **D** through intermediate **C** by nitrogen loss. Finally, hydrogen abstraction transfer (HAT) of the aminyl radical from surroundings gives the desired product **3a**. For carbon radical initiated cyclization, a similar sequential radical pathway is taken.

In conclusion, we have developed a novel and practical method for the synthesis of C2 diversified benzoimidazole derivatives from 1-azido-2-isocyanoarenes. This tandem process was triggered by adding various radical species to isocyanide, followed by cycloaddition of the resulting imidoyl radical intermediate to the azido group. Subsequent nitrogen loss and hydrogen abstraction transfer of the aminyl radical intermediate gave the final product. Carbon radicals generated from another annulation process could also be applied to this reaction, furnishing a structurally unique bisheterocyclic system containing both benzoimidazole and other heterocycles, such as dihydrobenzofurane, dihydrobenzothiophene, and indoline. Three chemical bonds were formed in order under mild conditions. Such kind of cycloaddition of an imidoyl radical to a heteroatom by forming a C−heteroatom bond is unprecedented. This methodology not only provides a practical approach

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to functionalized benzoimidazoles but also expands the synthetic application of the imidoyl radical in organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01339.

Experimental procedure; copies of ^{1}H, ^{13}C, or ^{31}P spectra for compounds (PDF)

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Notes

The authors declare no competing financial interest.

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