Organic LETTERS

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Oxidant-Switchable Selective Synthesis of 2-Aminobenzimidazoles via C−H Amination/Acetoxylation of Guanidines

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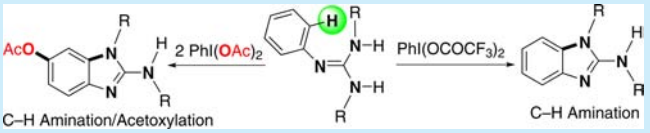
Supporting Information

ABSTRACT: The iodine(III) compound promoted C−H amination and tandem C−H amination/acetoxylation of guanidines are achieved for the first time to provide efficiently 2-aminobenzimidazoles and acetoxyl-substituted 2-aminobenzimidazoles, respectively. The amount and type of iodine(III) compounds control the selective syntheses of two types of 2-aminobenzimidazoles. This reaction shows good regioselectivity when unsymmetrical substrates are used.



The 2-aminobenzimidazole scaffold is found in a wide range of drug molecules for their unique biological activities (Figure 1),[1,2] so the construction of a substituted 2-aminobenzimidazole has received much attention. There are two classical methods to synthesize substituted 2-aminobenzimidazoles. The first one is the ring-closed condensation of (2-aminophenyl)thiourea between the NH_2 group and C═S bond.[3] The second one is the amination of benzimidazoles.[4] Recently, Cu- or Pd-catalyzed intramolecular C−X amination has been developed to construct 2-aminobenzimidazoles (Scheme 1).[5] In this strategy, transition metals are required, and halogen waste is produced. In addition, the *N*-substituent is usually an aryl and acyl group. The use of an alkyl group has rarely been reported.

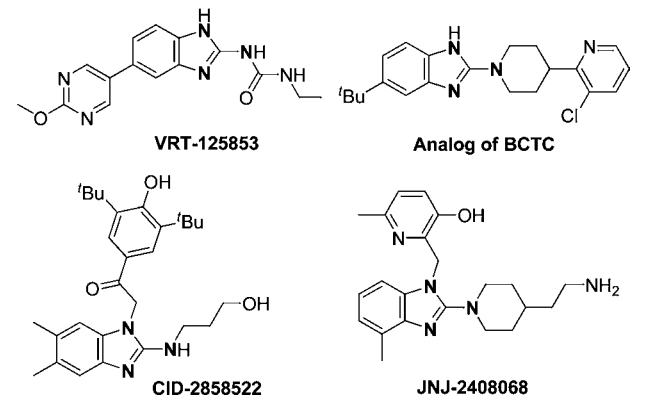
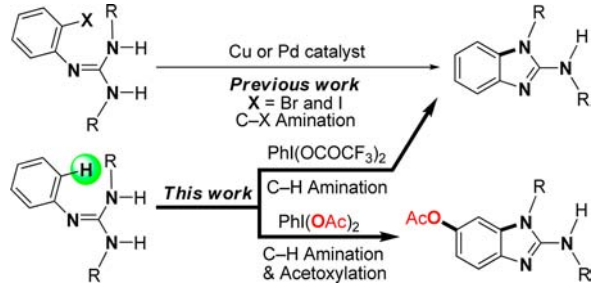


Figure 1. Representative examples of 2-aminobenzimidazoles with biological activities.

The oxidative C−H bond amination to construct a new C−N bond has experienced a rapid development because of their virtue of step-efficiency and atom-economy. Various transition metals including Pd,[6] Cu,[7] Ag,[8] and Rh[9] could catalyze this process. Recently, alternative metal-free C−H bond amination methods have also been developed.[10] Hypervalent iodine(III) compounds, owing to their useful oxidizing properties, environmental character, and commercial availability,[11] are widely used in the C−N bond formation.[12] The Zhu group[13b] and Long group[13d] developed the intramolecular C−N bond formation of amidine via iodine(III) compounds as oxidant to prepare benzimidazoles.[13] As far as we are aware, intramolecular metal-free aryl C−H amination and tandem C−H amination/benzene-ring acetoxylation of guanidines have not been reported.

Scheme 1. Synthesis of 2-Aminobenzimidazole via C−X or C−H Amination



We are interested in the synthesis and reactivity of guanidines.[14] Here, we report the iodine(III) compound promoted C−H amination and tandem C−H amination/acetoxylation of guanidines to prepare 2-aminobenzimidazoles and acetoxyl-substituted 2-aminobenzimidazoles, respectively. The amount and type of iodine(III) compounds control the selective syntheses of two types of 2-aminobenzimidazoles.

1,3-Diisopropyl-2-phenylguanidine **1a** was chosen as a model to perform this reaction. When 1.1 equiv of $PhI(OAc)_2$ was utilized as oxidant, benzimidazole **3a** was obtained in 31% yield. Gratifyingly, another product was an acetoxyl-substituted

Received: September 23, 2014
Published: December 4, 2014

   dx.doi.org/10.1021/ol502815p | *Org. Lett.* 2014, 16, 6274−6277

compound **2a** in 26% yield (Table 1, entry 1). The structure of **2a** was confirmed by X-ray crystallographic analysis (see the Supporting Information for the X-ray structure of **2a**). It clearly shows the acetoxyl group is selectively connected at the *para* position of the benzene ring on 1,3-diisopropyl-2-phenylguanidine **1a**. This result drew our interest because it simultaneously achieved the C−N bond formation and direct benzene acetoxylation. This acetoxylation process has not been reported in other benzimidazole synthesis from amidines via iodine(III) oxidant even though the excess of oxidant was utilized, and it reflects the different reactivity between amidine and guanidine compounds. What is more, there are mature strategies to change acetoxyl group to hydroxyl, alkoxyl, and aryl groups.[15] It can be used in the synthesis of more complex heterocyclic compounds.

Table 1. Condition Screening of C−H Amination/Acetoxylation of Guanidine 1a via $PhI(OAc)_2$

entry	solvent	*n*	temp (°C)	yield[a] (%) (**2a**)	yield[a] (%) (**3a**)
1	MeCN	1.1	80	26	31
2	C_6H_6	2.2	80	48	19
3	toluene	2.2	80	16	12
4	THF	2.2	80	67	trace
5	MeCN	2.2	50	59	15
6	MeCN	2.2	80	74	<5
7	MeCN	3.3	80	75	<5
8	EtOH	2.2	80	25	<5
9	AcOH	2.2	80	trace	trace

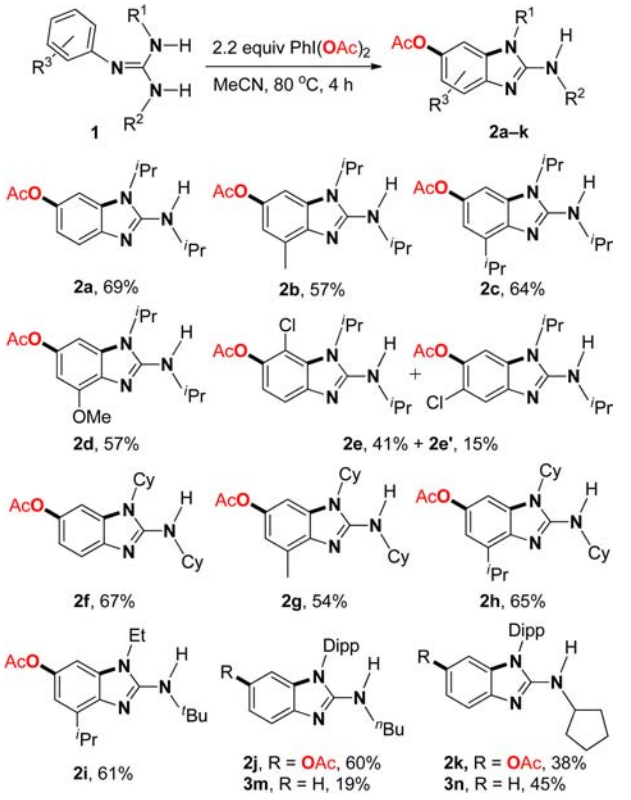
[a]GC yield.

Condition screening of C−H amination/acetoxylation of guanidine **1a** via $PhI(OAc)_2$ was carried out (Table 1). We found that **2a** could be obtained in 74% yield when the reaction was performed in MeCN at 80 °C for 4 h with 2.2 equiv of $PhI(OAc)_2$ (entry 6).

As summarized in Scheme 2, this C−H amination/acetoxylation method could be applied in various guanidines. 1,3-Dialkyl-2-arylguanidines were suitable substrates to proceed via C−H amination/acetoxylation to give the corresponding acetoxyl-substituted 2-aminobenzimidazoles **2a**−**k**. The *ortho*-substituents on the benzene ring could be tolerated under the present conditions (**2b**−**d** and **2g**,**h**). As for *meta*-substituents on the benzene ring, the products were two isomers (**2e** and **2e**′). When 1-*tert*-butyl-3-ethyl-2-phenylguanidine was utilized, the regioselective isomer **2i** was exclusively produced, probably owing to the steric hindrance of the *tert*-butyl group. When 1-butyl-3-(2,6-diisopropylphenyl)-2-phenylguanidine was applied in the reaction, the acetoxyl-substituted 2-aminobenzimidazole **2j** was formed as the major product with the acetoxyl-free byproduct **3m**. Interestingly, C−H amination occurred on the nitrogen atom adjoining to the bulky 2,6-diisopropylphenyl group (Dipp). In this process, this Dipp-N−H acidity probably played a vital part in the oxidative C−N formation.

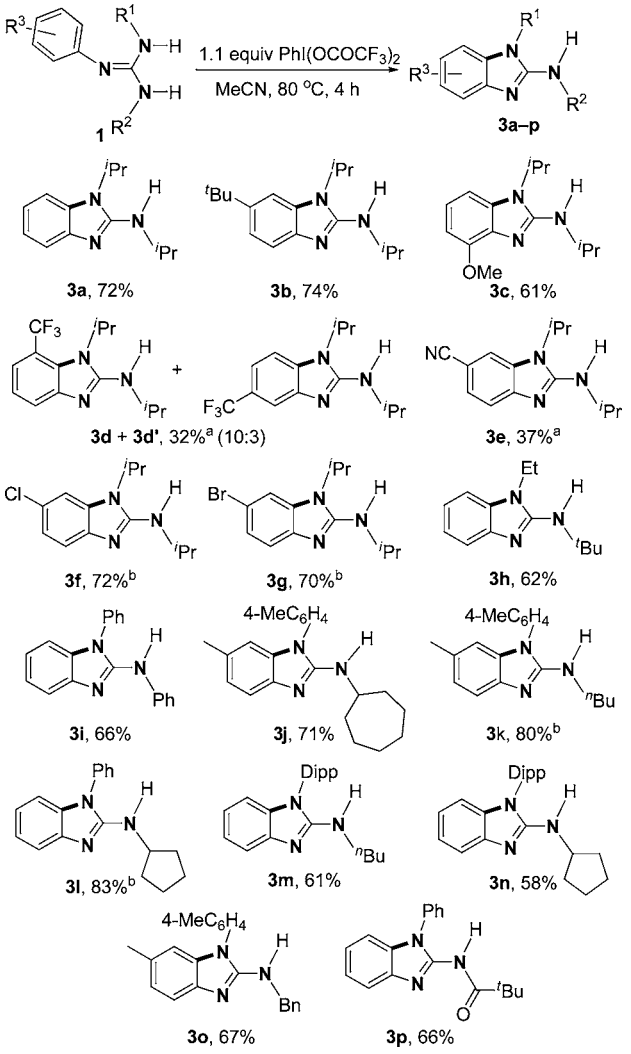
Unexpectedly, even if the excess of phenyliodine(III) bis(trifloroacetate) ($PhI(OCOCF_3)_2$) was utilized as an oxidant instead of $PhI(OAc)_2$, only 2-aminobenzimidazoles via the C−H amination were observed, but no trifluoroacetoxyl group was incorporated in the final products. Scheme 3 summarized the representative $PhI(OCOCF_3)_2$-promoted synthesis of 2-aminobenzimidazoles. Various guanidines, such as 1,3-dialkyl-2-arylguanidines, 1-alkyl-2,3-diarylguanidines, and 1,2,3-triarylguanidines, were tested in this method to afford the corresponding 2-aminobenzimidazoles **3a**−**p** in medium to high yields. Various EWG and EDG group could be tolerated, including methoxyl, trifluoromethyl, cyano, and halogen groups (**3c**−**g**). The *ortho*- or *para*-substituents on the benzene ring could be utilized, while the *meta*-substituents on the benzene ring led to two isomers as products (**3d** and **d**′). Similar to regioselectivity of **2i** in Scheme 2, **3h** could be exclusively obtained by the oxidative C−H amination. When 1-alkyl-2,3-diarylguanidines were applied in the reaction, C−H amination also occurred on the nitrogen atom adjoining to the aryl groups to regioselectively provide the corresponding products **3m**,**n**. The structure of the regioselective isomer **3n** was confirmed by single-crystal X-ray diffraction analysis (see the Supporting Information for the X-ray structure of **3n**). However, the guanidines without an *N*-substituent group could not be tolerated; for example, 1,2-diphenylguanidine PhN═C(NHPh)NH_2 was tested to give the oxidized azo compound. Thus, acyl chloride was utilized to protect the amino group to give guanidine PhN═C(NHPh)(NHCO^{t}Bu), which was further oxidized to provide the corresponding **3p**. When 1-aryl-2,3-dibenzylguanidines were utilized in this method, a complicated mixture was observed. Then 1,2-diaryl-3-dibenzylguanidine was tested to give Bn-substituted 2-aminobenzimidazole **3o**. The compounds **3o** and **3p** have the potential application to give 2-aminobenzimidazoles with free NH_2. Only **3l** free of acetoxylation product was obtained when 1.1 equiv of $PhI(OAc)_2$ was used as oxidant, probably because the PhN−H acidity played an important role in this process.

Scheme 2. Synthesis of Acetoxyl-Substituted 2-Aminobenzimidazoles 2a−k



dx.doi.org/10.1021/ol502815p | *Org. Lett.* 2014, 16, 6274−6277

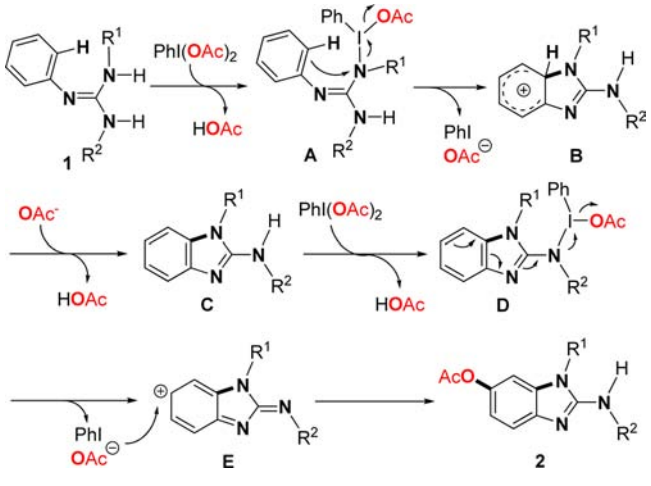
Scheme 3. Synthesis of 2-Aminobenzimidazoles 3a−p



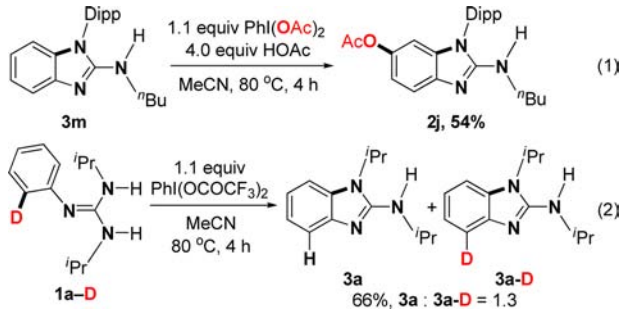
[a]Heated for 8 h. [b]1.1 equiv of $PhI(OAc)_2$ used as oxidant.

A tentative mechanism for the formation of acetoxyl-substituted 2-aminobenimidazoles **2** is proposed in Scheme 4. The first step is the oxidation of one N−H bond in guanidines by $PhI(OAc)_2$ with the release of one molecule of HOAc. When R^1 = aryl and R^2 = alkyl, the oxidation of N−H bond regioselectively takes place the nitrogen atom attached the aryl group. Then the electron-deficient N atom in **A** is attacked by the benzene ring to obtain the cationic intermediate **B**. Intermediate **B** undergoes the aromatization to yield 2-aminobenimidazole intermediate **C**, which remains one N−H bond. The next step is the acetoxylation process.[16] Intermediate **C** can be further oxidized by the second molecule of $PhI(OAc)_2$ to provide intermediate **D**. The cationic intermediate **E** can accept the nucleophilic attack of OAc^- and rearomatize to give the final product **2**.

Scheme 4. Proposed Mechanism for the Synthesis of Compound 2



In order to gain information on this mechanism, the isolated 2-aminobenzimidazole **3m** was allowed to react with $PhI(OAc)_2$ in MeCN at 80 °C with the addition of 4 equiv of HOAc (eq 1).



The yield of **2j** was 54%. This result clearly showed that acetoxyl-substituted 2-aminobenimidazoles **2** could be obtained from the intermediate **C** in Scheme 4. Furthermore, the deuterium experiment was carried out. The reaction of **1a-D** under the standard conditions could provide a mixture of the products **3a-D** and **3a** in 66% combined yields, and the ratio of **3a**:**3a-D** was 1.3 (eq 2). This KIE value reveals that the C−H bond cleavage is not the rate-determining step in this reaction.

In summary, we have developed the efficient, metal-free methods to prepare 2-aminobenzimidazoles and acetoxyl-substituted 2-aminobenimidazoles by the iodine(III) compound promoted C−H amination and tandem C−H amination/acetoxylation of guanidines, respectively. The amount and type of iodine(III) compounds control the selective syntheses of two types of 2-aminobenzimidazoles. This reaction shows good regioselectivity when unsymmetrical substrates are used.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, X-ray data for **2a** and **3n** (CIF), and scanned NMR spectra of all new products. 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.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China and the "973" program from National Basic Research Program of China (2011CB808601).

dx.doi.org/10.1021/ol502815p | Org. Lett. 2014, 16, 6274−6277

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