Organic LETTERS

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Copper-Promoted Cycloaddition of α-Methylenyl Isocyanides with Benzothiazoles: Tunable Access to Benzo[*d*]imidazothiazoles

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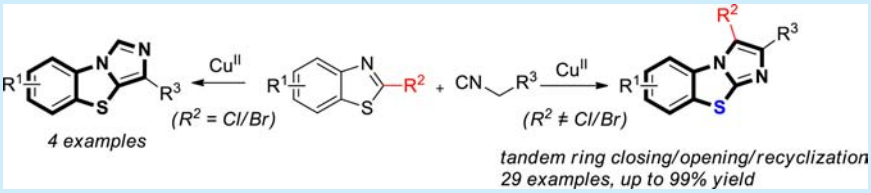
Supporting Information



ABSTRACT: A tunable route to both isomers of benzo[*d*]imidazothiazole has been developed through copper-promoted cycloaddition of α-methylenyl isocyanides with benzothiazoles. When the C2 position of benzothiazole is linked to a C−H or C−C bond, benzo[*d*]imidazo[2,1-*b*]thiazoles are obtained through a novel rearrangement via C−S bond cleavage and formation of a new C−S bond. When 2-chloro- or 2-bromobenzothiazoles are used under the same reaction conditions, the isomeric benzo[*d*]imidazo[5,1-*b*]thiazoles are formed selectively. These reactions proceed smoothly in moderate to excellent yields at room temperature, and a wide range of functional groups are tolerated.

Both imidazole[1] and thiazole[2] are essential five-membered two-heteroatom-containing heterocycles which can be found in numerous natural products, pharmaceutical agents, and functional chemicals. Benzo[*d*]imidazothiazole, a tricyclic fused scaffold containing both imidazole and thiazole, exists in two isomeric forms, benzo[*d*]imidazo[2,1-*b*]thiazole (**A**) and benzo[*d*]imidazo-[5,1-*b*]thiazole (**B**) (Scheme 1). Although there is little difference between the structures, the two isomers have distinctive bioactivities,[3,4] and the synthetic routes leading to them are totally different. For example, methyl benzo[*d*]-imidazo[2,1-*b*]thiazole-2-carboxylate (**A1**) is a potential non-sedative anxiolytic (IC_{50} = 60 nM).[5] A more complicated derivative (**A2**) was found to be highly active against FMS-like tyrosine kinase-3 (FLT3) and has entered phase II clinical trials.[6] The other isomer, benzo[*d*]imidazo[5,1-*b*]thiazole (**B**), is found as a core unit in the potent phosphodiesterase inhibitor E10A (**B1**).[4] Traditional synthetic approaches to **A** are mainly based on cyclo-condensation of 2-aminobenzothiazole with α-bromo or α-iodo carbonyl derivatives in ethanol under reflux.[5,7] The synthesis of **B**, however, uses C2-aminoalkylated benzothiazoles as key intermediates prepared in four steps starting from 2-amino-benzothiazoles.[4] In such a lengthy synthetic route, harsh conditions, such as use of lithium diisoproplyamide at −78 °C and $POCl_3$ at high temperatures, are applied. In this paper, we report tunable access to both **A** and **B** through copper-promoted cycloaddition of α-methylenyl isocyanides to benzothiazoles at room temperature. The selectivity is controlled solely by the substituent on the C2 position of the benzothiazole.

α-Isocyanoacetates, the most frequently used representatives of α-methylenyl isocyanide,[8] have been studied extensively in the construction of five-membered *N*-containing heterocycles through [3 + 2] cycloadditions with aldehydes/ketones,[9] imines[10] activated alkenes,[11] allenoates,[12] alkynes,[13] and aryl isocyanides.[14] Recently, other modes of reactions, such as [3 + 3],[15] [3 + 2 + 1],[16] and [6 + 3][17] cycloadditions have also been reported, enriching the reactivity of α-isocyanoacetates as unique 1,3-dipolar species. Although rearrangement-based cycloaddition involving α-isocyanoacetates is much less common, it could lead to complex structures in a single operational step. For example, Liu has reported the synthesis of two-carbon-tethered pyrrole/oxazole pairs,[18] pyrrolizidines,[19] and tricyclic indolizidine alkaloids[20] by the reaction of α-isocyanoacetates with α-alkenoyl ketene dithioacetals. Since known routes to the synthesis of benzo[*d*]imidazo[5,1-*b*]thiazoles (**B**) were less efficient,[4] a straightforward strategy through [3 + 2] cycloaddition of benzothiazoles and α-isocyanoacetates was designed (Scheme 1). A cyclized product was obtained by mixing benzothiazole and ethyl α-isocyanoactate in the presence of $Cu(OAc)_2$ and a base, Cs_2CO_3. Intriguingly, its structure was finally identified, and unambiguously confirmed by X-ray analysis as ethyl benzo[*d*]-imidazo[2,1-*b*]thiazole-2-carboxylate **3a**, an isomer of the originally designed product. This unexpected rearrangement prompted a detailed study of this reaction.

The reaction conditions were optimized with benzothiazole (**1a**) and ethyl α-isocyanoactate (**2a**) as model reactants, and ethyl benzo[*d*]imidazo[2,1-*b*]thiazole-2-carboxylate (**3a**) was obtained in 51% yield in the presence of $Cu(OAc)_2$ (1.5 equiv) and Cs_2CO_3 (1.0 equiv) in DMSO at 90 °C (entry 1, Table 1). Other solvents such as MeCN and dioxane were less effective, and the reaction was completely suppressed in toluene (entries 2−4).

Received: September 16, 2015
Published: October 28, 2015

DOI: 10.1021/acs.orglett.5b02694
Org. Lett. 2015, 17, 5336−5339

Scheme 1. Synthesis of Benzo[*d*]imidazothiazoles

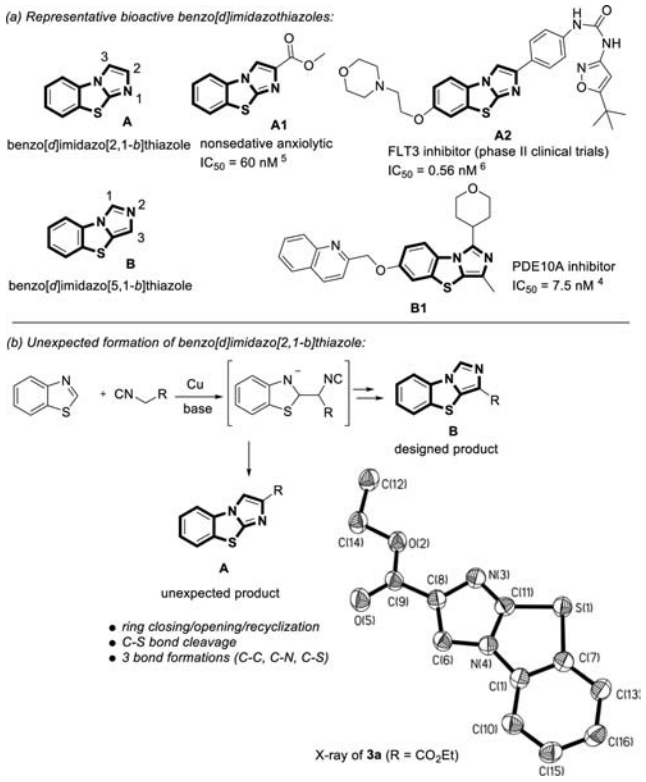
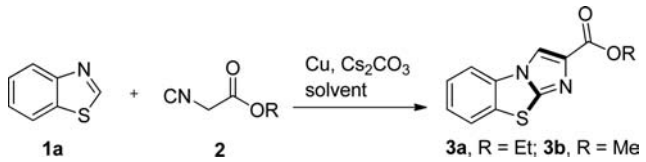


Table 1. Optimization of Reaction Conditions[a]



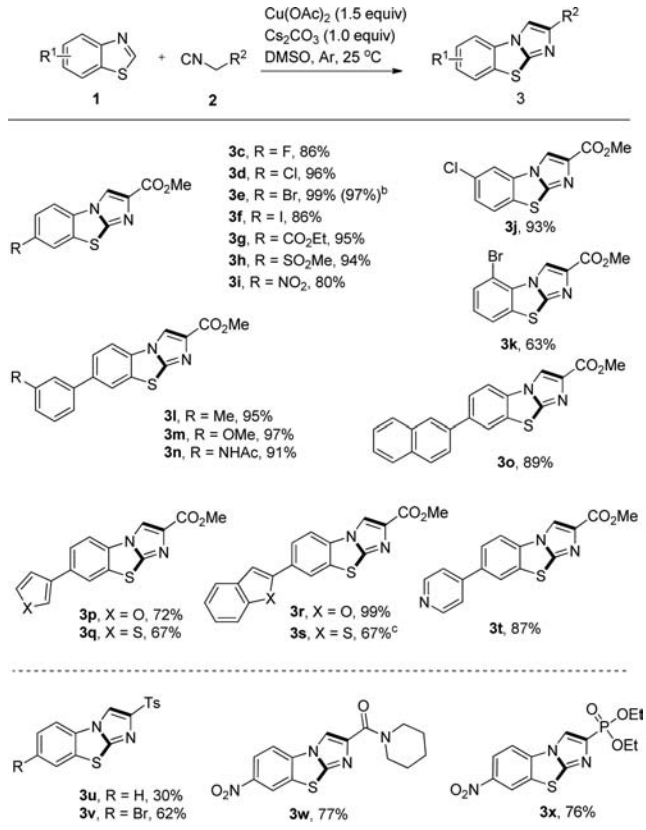
entry	Cu	R	solvent	temp (°C)	time (h)	yield[b] (%)
1	$Cu(OAc)_2$	Et	DMSO	90	1	51
2	$Cu(OAc)_2$	Et	MeCN	90	1	20
3	$Cu(OAc)_2$	Et	dioxane	90	1	16
4	$Cu(OAc)_2$	Et	toluene	90	1	0
5	$Cu(acac)_2$	Et	DMSO	90	1	21
6	$Cu(TFA)_2$	Et	DMSO	90	1	0
7	$Cu(OAc)_2$	Et	DMSO	70	4	67
8	$Cu(OAc)_2$	Et	DMSO	50	4	61
9	$Cu(OAc)_2$	Et	DMSO	25	4	50
10	$Cu(OAc)_2$	Et	DMSO	25	4[c]	71
11	$Cu(OAc)_2$[d]	Et	DMSO	25	4[c]	40
12	**$Cu(OAc)_2$**	**Me**	**DMSO**	**25**	**4[c]**	**91**

[a]Reaction conditions: benzothiazole **1a** (0.2 mmol), α-isocyanoacetate **2** (0.4 mmol, 2.0 equiv), [Cu^{2+}] (0.3 mmol, 1.5 equiv), Cs_2CO_3 (0.2 mmol, 1.0 equiv), 2.0 mL of solvent, in Ar. [b]Isolated yield of **3**. [c]A solution of **2** in 1.0 mL of DMSO was added to the reaction mixture during 4 h via a syringe pump and the mixture allowed to react for a further 20 h. [d]1.0 equiv.

Other copper salts were also tested but showed much less efficiency or no activity at all in promoting the reaction (entries 5 and 6). Conducting the reaction at room temperature can also give the product **3a** in 50% yield (entry 9). The yield of **3a** was increased to 71% when a solution of **2a** in 1 mL of DMSO was introduced to the reaction mixture via a syringe pump during 4 h and the total reaction time was extended to 24 h (entry 10). The yield was decreased sharply to 40% with a reduced amount of $Cu(OAc)_2$ (1.0 equiv, entry 11). Simply by changing **2a** to methyl α-isocyanoacetate (**2b**), the corresponding product **3b** was generated in excellent yield (91%, entry 12). In addition, only trace amount of the product was detected when the reaction was conducted in air (result not shown in Table 1).

With the optimized conditions in hand, the scope of the benzothiazoles was investigated in reactions with methyl α-isocyanoacetate (**2b**) (Scheme 2). Benzothiazoles halogenated

Scheme 2. Substrate Scope of the Reaction[a]



[a]Reaction conditions: **1** (0.2 mmol), $Cu(OAc)_2$ (0.3 mmol, 1.5 equiv), Cs_2CO_3 (0.2 mmol, 1.0 equiv), DMSO (1 mL), 25 °C, in Ar. A solution of **2** (0.4 mmol) in 1.0 mL of DMSO was added to the reaction mixture during 4 h via a syringe pump, and allowed to react for a further 20 h. [b]5 mmol scale. [c]5 mL of DMSO in total (4 + 1 mL).

(F, Cl, Br, I) or substituted with other electron-withdrawing groups (CO_2Et, SO_2Me, and NO_2) at the 6 position underwent this transformation efficiently, generating the corresponding products in good to excellent yields (**3c–i**). The more sterically hindered 4-bromobenzothiazole was less reactive (**3k**). Benzothiazoles bearing functionalized aromatic or heteroaromatic rings, including naphthalene, (benzo)furan, (benzo)thiophene, and pyridine, were well tolerated under the standard conditions (**3l–t**). It is noteworthy that the gram-scale preparation of **3e** was equally efficient.

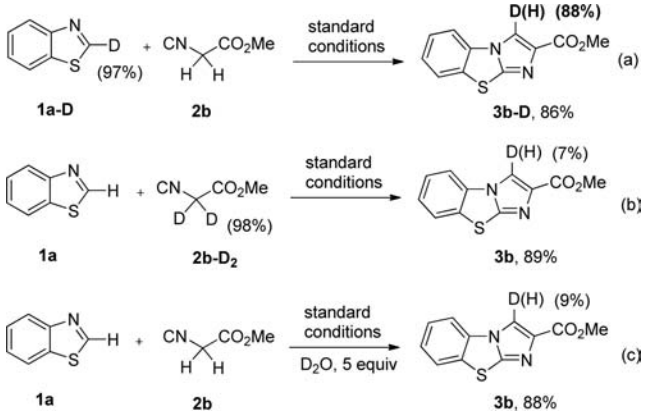
α-Methylenyl isocyanides activated by other electron-withdrawing groups can also undergo this unique cycloaddition reaction (Scheme 2). For example, 7-bromo-2-tosylbenzo[*d*]-imidazo[2,1-*b*]thiazole (**3v**) was obtained in 62% yield when tosylmethyl isocyanide **2c** was used. Further, amide and phosphate could also serve as activating groups of α-methylenyl isocyanides in condensations with 6-nitrobenzothiazole, afford-

DOI: 10.1021/acs.orglett.5b02694
Org. Lett. 2015, 17, 5336–5339

ing **3w** and **3x** in good yields. However, no product was formed when the nonsubstituted benzothiazole (**1a**) was used as a reaction partner. When benzoxazole or benzimidazole was used in the reaction, no corresponding products were generated.

To gain insight into how the unexpected scaffold was formed, the deuteration studies shown in Scheme 3 were performed.

Scheme 3. Deuteration Studies



When benzothiazole **1a-D**, substituted with deuterium at position C2 (97% D), was applied in a standard reaction with **2b**, about 88% of the product **3b** was found to be deuterated at the C3 position. However, use of dideuteromethyl α-isocyanoacetate (**2b-D$_2$**) or addition of 5 equiv of D_2O to the reaction with **1a** led to deuteration rates of only 9% and 7%, respectively. These results clearly indicate that the C3 carbon in **3b** and the associated hydrogen originate from C2 of benzothiazole.

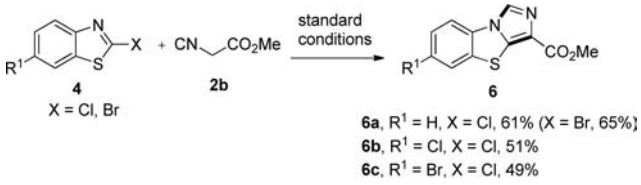
To further confirm the phenomena observed in the deuteration studies, 2-methylbenzothiazole **4a** was tested in a reaction with **2b**, but this resulted in none of the desired product (Scheme 4). When the more reactive 2-methyl-6-nitrobenzo-

Scheme 4. Reactions of C2-Substituted Benzothiazoles with 2b

thiazole was used, the corresponding product (**5b**) was generated in 91% yield, providing strong evidence of the origin of the C3 carbon of scaffold **A**. Furthermore, the CF_2H-, CF_3-, and CF_2Cl-substituted methyl benzo[*d*]imidazo[2,1-*b*]thiazole-2-carboxylates (**5c**−**e**) were also obtained in moderate yields. These methyl and fluoromethyl derivatives, which are not readily available by conventional methods, are expected to be interesting candidates in related biological studies.[5,7]

When 2-chloro- or 2-bromobenzothiazole was subjected to the same reaction, an isomeric structure of **3b**, benzo[*d*]imidazo[5,1-*b*]thiazole (**6a**), was generated selectively in moderate yield (Scheme 5). Brief substrate extension showed that functional groups such as Cl/Br were tolerated in the formation of **6b**,**c**, albeit in relatively lower yields. Obviously, no rearrangement was taking place in this case, and thus, both isomers of benzo[*d*]-imidazothiazole (**A**) and (**B**) could be accessed selectively under

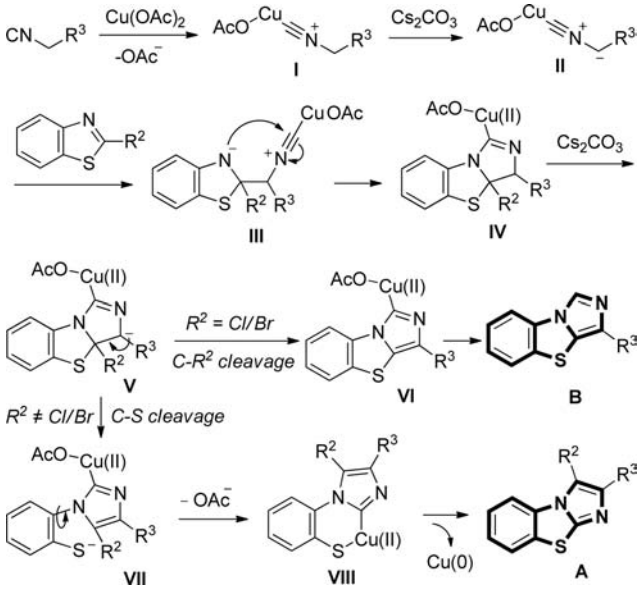
Scheme 5. Selective Access to Benzo[*d*]imidazo[5,1-*b*]thiazole B



mild conditions, controlled simply by the substituent on C2 of the benzothiazole substrate.

Although the frameworks of **A** and **B** are totally different, their formation can be rationalized by the following scheme in which some common intermediates are shared (Scheme 6). Initially,

Scheme 6. Proposed Mechanism



deprotonation of the methylenyl group takes place in the presence of Cs_2CO_3, enabled by both the electron-withdrawing ester group and the Cu(II)-coordinated isocyano moiety. Subsequently, nucleophilic addition of the carbon anion in intermediate **II** to the C2 carbon of benzotiazole generates the adduct **III** followed by intramolecular addition of the nitrogen-centered anion to the nitrilium moiety. The cyclized intermediate **IV** is deprotonated again to produce a common intermediate **V** for individual pathways directed toward the formation of **A** and **B**. When R is Cl or Br, the carbon−halogen bond breaks preferentially to give the initially designed structure **B** via [3 + 2] cycloaddition. When R is H or C, the corresponding C−H or C−C cleavage must overcome much higher energy barriers, and as a result, the weaker C−S bond cleaves to give a ring opened intermediate **VII**. Subsequently, the resulting sulfur anion attacks the copper center to furnish a six-membered cyclic cuprate **VIII**, and finally, reductive elimination generates the rearranged structure **A** through a process involving C−C and C−N bond formation followed by C−S bond cleavage and a new C−S bond formation.

In conclusion, we have developed a novel and practical Cu-promoted cycloaddition of benzothiazoles and α-methylenyl isocyanides, affording benzo[*d*]imidazo[2,1-*b*]thiazoles and benzo[*d*]imidazo[5,1-*b*]thiazoles selectively under mild con-

DOI: 10.1021/acs.orglett.5b02694
Org. Lett. 2015, 17, 5336−5339

ditions. The tandem ring-closing/opening/recyclization rearrangement involving C−S bond cleavage and formation of three new bonds (C−C, C−N, C−S) provides convenient access to benzo[*d*]imidazo[2,1-*b*]thiazoles when the C2 position of benzothiazole is linked to a C−H or C−C bond. When 2-chloro- or 2-bromobenzothiazoles are used under the same reaction conditions, the isomeric benzo[*d*]imidazo[5,1-*b*]thiazoles are formed selectively. The reactions were carried out at room temperature with moderate to excellent yields, and a wide range of functional groups are tolerated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02694.

General experimental procedure, characterization data of the compounds (PDF) and X-ray crystallographic data for **3a** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Science Foundation of China (21272233, 21472190).

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DOI: 10.1021/acs.orglett.5b02694
Org. Lett. 2015, 17, 5336−5339