Organic LETTERS

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Copper-Catalyzed Intermolecular Aminoazidation of Alkenes

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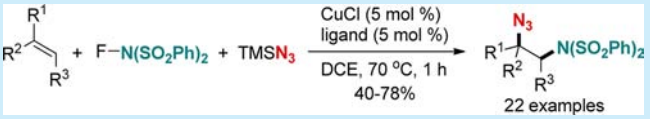
Supporting Information

ABSTRACT: Copper-catalyzed intermolecular aminoazidation of alkenes is described. This novel methodology provides an efficient approach to vicinal amino azides which can easily be transformed into other valuable amine derivatives. The commercially available *N*-fluorobenzenesulfonimide (NFSI) is used as a nitrogen-radical precursor and $TMSN_3$ as the N_3 source. Yields are moderate to excellent, and for internal alkenes aminoazidation occurs with excellent diastereoselectivity.



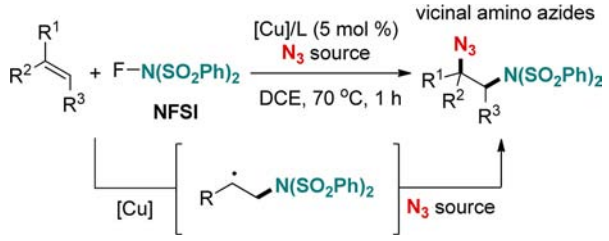
Organic azides are highly important and valuable compounds which have gained great attention not only because of their widespread application as versatile intermediates and building blocks in organic synthesis but also because of their remarkable biological activity.[1] Moreover, azides have been intensively used as reactive functionalities in materials science,[2] supramolecular chemistry,[3] medicinal chemistry[4] and biotechnology.[5] Along these lines, the Cu-catalyzed [3 + 2] cycloaddition of an azide with an alkyne as the bona fide click reaction has recently emerged as a powerful tool in drug discovery.[6] In light of the importance of this compound class, there is continuing interest in the development of novel synthetic methods for C−N_3 bond formation.

As part of our ongoing interest in intermolecular vicinal radical difunctionalization of alkenes, we recently reported radical azidooxygenation,[7a] oxyarylation[7b] trifluoromethylaminoxylation,[7c] and hydroxyarylation.[7d] Encouraged by these results, we became interested in the development of other radical alkene difunctionalization processes. Considering the importance of the azide and the amino group, we planned to introduce these two functionalities sequentially in a cascade process allowing the straightforward preparation of vicinal amino azides. To the best of our knowledge, intermolecular vicinal aminoazidation has not been reported to date.[7e]

We envisioned to use a radical approach where a nitrogen-centered radical adds to an alkene providing a C-radical which then undergoes azidation.[8] First results on a copper-catalyzed intermolecular aminoazidation of alkenes using commercially available *N*-fluorobenzenesulfonimide (NFSI) as nitrogen-radical precursor and $TMSN_3$ as N_3 source leading to vicinal amino azides are disclosed herein (Scheme 1).

Recently, much attention has been paid to transition-metal-catalyzed difunctionalization of alkenes.[9] Such reactions allow direct vicinal installation of two functional groups across a C−C double bond. Among these reactions, difunctionalization of alkenes, comprising a C−N bond formation, is particularly interesting allowing the synthesis of important nitrogen-containing compounds. Examples are diamination,[10] aminooxygenation,[11] aminohalogenation,[12] and carboamination.[13] The intramolecular aminative difunctionalization of alkenes has been intensively investigated. In our eyes, intermolecular variants are more attractive but certainly far more challenging. Therefore, development of new methods for intermolecular aminative difunctionalization of alkenes is important.

Scheme 1. Copper-Catalyzed Intermolecular Aminoazidation of Alkenes

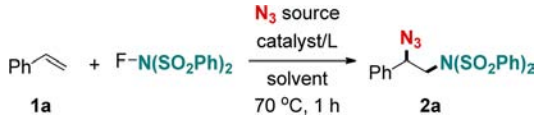


We decided to use NFSI as the N-radical precursor because it has been already demonstrated that the bisphenylsulfonylamidyl radical can be generated by reaction of NFSI with Cu(I) salts.[13a,b] $TMSN_3$ was chosen as the commercially available N_3 source. Aminoazidation of styrene **1a** in the presence of CuCl as catalyst in DCE at 70 °C under argon atmosphere was investigated first. Unfortunately, only traces of the targeted product **2a** were identified (Table 1, entry 1). Studies were continued by screening various additives **L1**−**L5**. Pleasingly, the yield was significantly improved (57−78%), and 1,10-phenanthroline **L1** turned out to be well-suited, affording **2a** in 78% yield (Table 1, entries 2−6). Solvent effects were investigated, and we found that DCE is the best solvent for this transformation. Other solvents, such as CH_3CN, dioxane, and DMF provided worse results (Table 1, entries 7−9). Next, a series of Cu(I) salts were tested. CuBr, CuI, CuOAc, $[(MeCN)_4Cu]PF_6$, and CuTc provided **2a** in 55−74% yield showing that CuCl performs slightly better (Table 1, entries 10−14). As compared to $TMSN_3$, alternative N_3 reagents, such as NaN_3, TsN_3, and DPPA afforded lower yields of **2a** (Table 1, entries 15−17). The reaction did not work at room

Received: February 18, 2014
Published: March 3, 2014

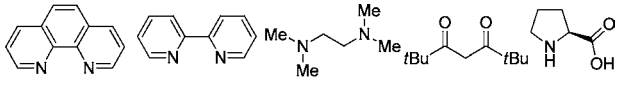
dx.doi.org/10.1021/ol500513b | *Org. Lett.* 2014, 16, 1790−1793

Table 1. Reaction Optimization Using Styrene as Substrate[a]



entry	catalyst	ligand	N_3 source	solvent	yield[b] (%)
1	CuCl	none	$TMSN_3$	DCE	trace
2	CuCl	**L1**	$TMSN_3$	DCE	78
3	CuCl	**L2**	$TMSN_3$	DCE	75
4	CuCl	**L3**	$TMSN_3$	DCE	58
5	CuCl	**L4**	$TMSN_3$	DCE	76
6	CuCl	**L5**	$TMSN_3$	DCE	57
7	CuCl	**L1**	$TMSN_3$	CH_3CN	56
8	CuCl	**L1**	$TMSN_3$	dioxane	52
9	CuCl	**L1**	$TMSN_3$	DMF	0
10	CuBr	**L1**	$TMSN_3$	DCE	74
11	CuI	**L1**	$TMSN_3$	DCE	70
12	CuOAc	**L1**	$TMSN_3$	DCE	55
13	$[(MeCN)_4Cu]PF_6$	**L1**	$TMSN_3$	DCE	68
14	CuTc	**L1**	$TMSN_3$	DCE	74
15	CuCl	**L1**	NaN_3	DCE	trace
16	CuCl	**L1**	TsN_3	DCE	trace
17	CuCl	**L1**	DPPA	DCE	20
18[c]	CuCl	**L1**	$TMSN_3$	DCE	0
19[d]	**CuCl**	**L1**	**$TMSN_3$**	**DCE**	**78**
20[e]	CuCl	**L1**	$TMSN_3$	DCE	0
21	none	**L1**	$TMSN_3$	DCE	0

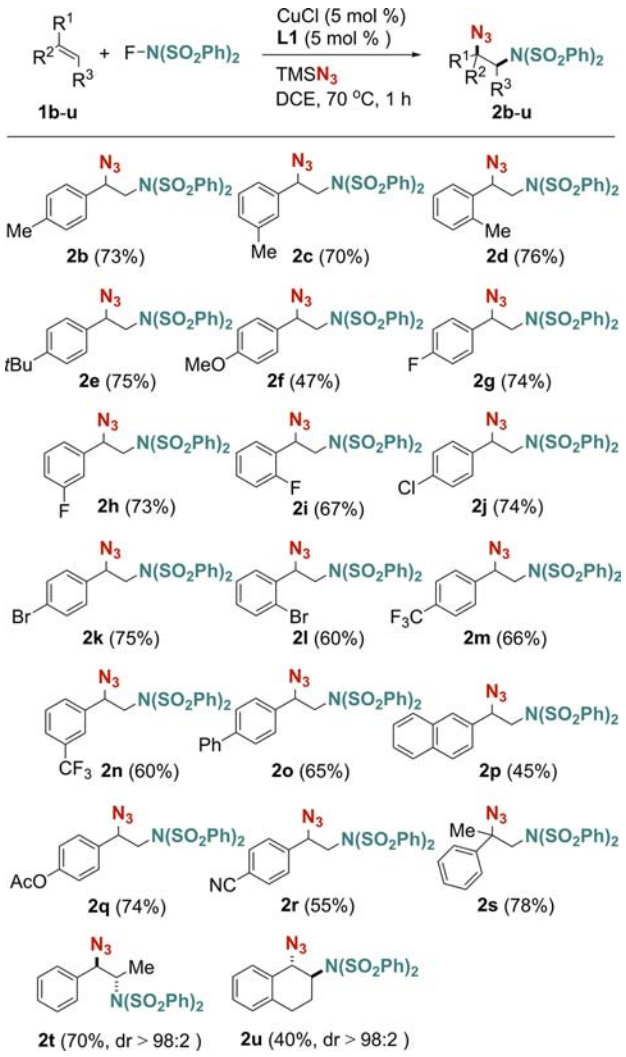
[a]Reaction conditions: **1a** (0.25 mmol), catalyst (10 mol %), ligand (10 mol %), N_3 source (0.375 mmol), and NFSI (0.375 mmol) in solvent (1.0 mL) at 70 °C under argon for 1 h. [b]Isolated yields. [c]The reaction was conducted at rt. [d]Using 5 mol % of CuCl and 5 mol % of **L1**. [e]Using 2 mol % of CuCl and 2 mol % of **L1**. DPPA = diphenylphosphoryl azide.



temperature (Table 1, entry 18). Catalyst and ligand loading could be lowered to 5 mol % without affecting the yield (Table 1, entry 19). However, the reaction did not work by using 2 mol % of catalyst and ligand (Table 1, entry 20). In addition, the reaction did not proceed in the absence of copper catalyst (Table 1, entry 21). These results imply that both the copper catalyst and ligand are essential for alkene aminoazidation (Table 1, entries 1 and 21).

With optimized reaction conditions in hand, we next explored the scope of the aminoazidation reaction (Scheme 2). Styrene derivatives bearing electron-donating substituents at the *p*-position of the arene ring provided the vicinal amino azides **2b** (4-Me), **2e** (4-*t*-Bu), and **2f** (4-MeO) in moderate to excellent yields (47−75%). *Ortho*- and *meta*-substituted congeners of **1b** gave similar results (**2c**,**d**). Styrene derivatives carrying halogen substituents such as F, Cl, and Br were successfully converted to the corresponding protected amino azides **2g**−**l** in good to excellent yields (60−75%). Substrates bearing other electron-withdrawing substituents, such as CF_3, OAc, and CN underwent vicinal difunctionalization smoothly to provide the corresponding products in moderate to good yields (**2m**: 66%, **2n**: 60%, **2q**: 74%, **2r**: 55%). *p*-Vinylbiphenyl afforded 65% of **2o**, and a slightly lower yield was obtained with 2-vinylnaphthalene (**2p**: 45%). In addition, we could show that

Scheme 2. Copper-Catalyzed Intermolecular Aminoazidation of Alkenes: Scope[a,b]



[a]Reaction conditions: **1b**−**u** (0.25 mmol), CuCl (5 mol %), **L1** (5 mol %), $TMSN_3$ (0.375 mmol), and NFSI (0.375 mmol) in DCE (1.0 mL) at 70 °C under argon for 1 h. [b]Isolated yields.

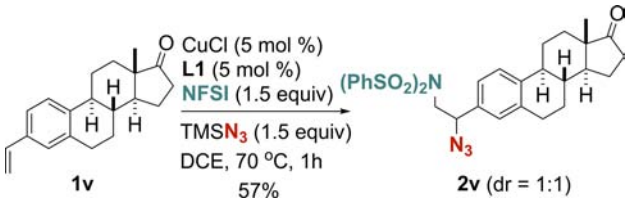
formation of quaternary C centers is possible using this novel method (see **2s**: 78%).

To address the diastereoselectivity, we investigated the aminoazidation of internal alkenes (Scheme 2). The selectivity was readily determined by ^1H NMR analysis of the crude product. *β*-Methylstyrene reacted under optimized conditions with complete regioselectivity to **2t**, which was isolated in 70% yield. Pleasingly, **2t** was formed with excellent diastereoselectivity (19:1). For assignment of the relative configuration we transformed **2t** to the known diamine **5** (see below). The selectivty can be explained by considering the allylic A[1,3] strain model.[14] Dihydronaphthalene reacted with excellent *trans*-selectivity (>98:2) and complete regioselectivity to provide the corresponding products **2u** in moderate yield. Unfortunately, aliphatic alkenes such as 1-heptene did not react under the optimized conditions.

We further applied the novel protocol to an estrone derivative **1v**, which was smoothly converted to corresponding product **2v** in 57% yield with 1:1 diastereoselectivity (Scheme 3).

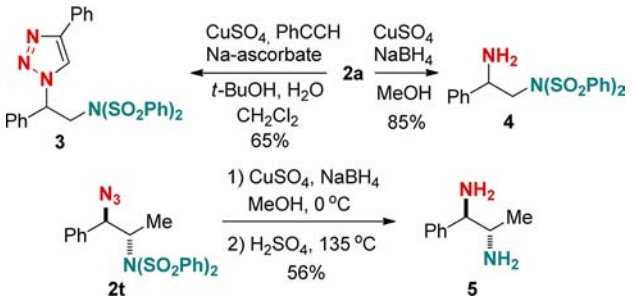
dx.doi.org/10.1021/ol500513b | *Org. Lett.* 2014, 16, 1790−1793

Scheme 3. Aminoazidation of an Estrone Derivative



To illustrate the synthetic utility of the aminoazidation products, we next investigated the follow-up chemistry (Scheme 4). Click reaction of **2a** with phenylacetylene using

Scheme 4. Transformations of 2a and 2t

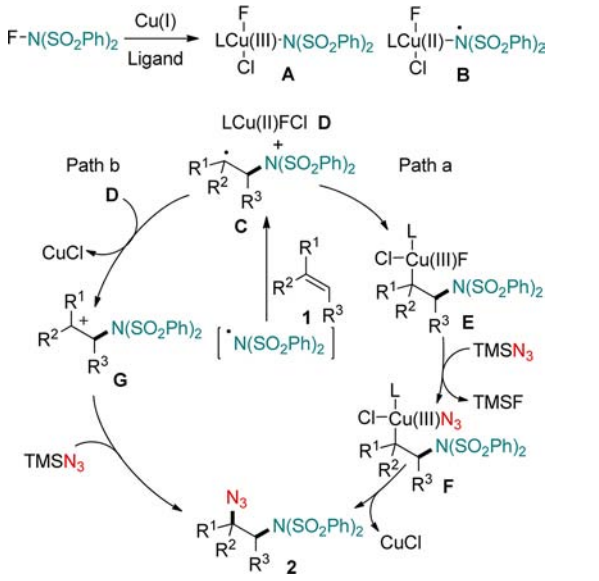


$CuSO_4$ as a catalyst provided triazole **3** in 65% yield. Azide reduction was easily achieved by treating **2a** with $CuSO_4$/$NaBH_4$ in MeOH at 0 °C to afford the monoprotected 1,2-diamine **4** in good yield (85%). It is important to note that both sulfonyl protecting groups in the bissulfonamides can be readily removed under acidic conditions.[10a,15] Amino azide **2t** was converted to 1,2-diamine **5** by azide reduction and subsequent desulfonylation (56% overall yield). The *trans*-configuration was assigned by comparing NMR data of **5** with known literature values.[16] In analogy, **2u** was transformed to the corresponing *trans*-1,2-diamine (38%, not shown). 1,2-Diamines are important functional groups present in various natural products, in biologically active compounds, and as ligands in metal catalysts.[10,17] Hence, our novel protocol provides an alternative and complementary approach to 1,2-diamines.

A plausible reaction mechanism is illustrated in Scheme 5. As previously suggested,[13a,b] CuCl first reduces NFSI to provide a Cu(III) species **A**[18] which could exist in equilibrium with a Cu(II)-stabilized N-centered radical **B**.[13a,b,19] Both are sources of the bis-sulfonylamidyl radical, which adds to the alkene to generate radical **C** along with the Cu(II) species **D**. In addition, **B** could react as complexed N-radical with the alkene. Two probable routes have to be considered. In path a, trapping of **C** with **D** provides Cu(III) species **E**, which undergoes ligand exchange with $TMSN_3$ to give Cu(III) complex **F** and TMSF. Reductive elimination of **F** eventually affords **2**, thereby regenerating the Cu(I) catalyst. Direct amidocupration of the alkene with **A** to **E** can be excluded since only the *trans*-product was obtained for aminoazidation of **1u**. Alternatively, in path b, **C** gets oxidized by **D** to a cationic intermediate **G** which is trapped by $TMSN_3$ to form **2**.[20]

In summary, we have presented a practical Cu-catalyzed intermolecular aminoazidation of alkenes using the commercially available NFSI and $TMSN_3$ as reagents. Aminoazidation of internal alkenes occurs with excellent diastereoselectivity, and products can be easily transformed into other valuable

Scheme 5. Proposed Reaction Mechanism



amine derivatives. Further studies on the synthetic applications and the mechanism are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data for the 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

We thank the Deutsche Forschungs-gemeinschaft (DFG) for supporting our work.

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