OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

From Alkenes to Isoxazolines via Copper-Mediated Alkene Cleavage and Dipolar Cycloaddition

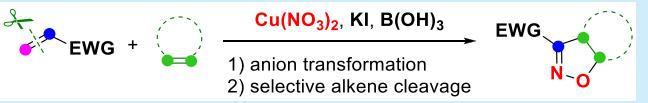
Mingchun Gao,[†,§] Yuansheng Gan,[†,§] and Bin Xu*[,†,‡]

[†]Department of Chemistry, Innovative Drug Research Center, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

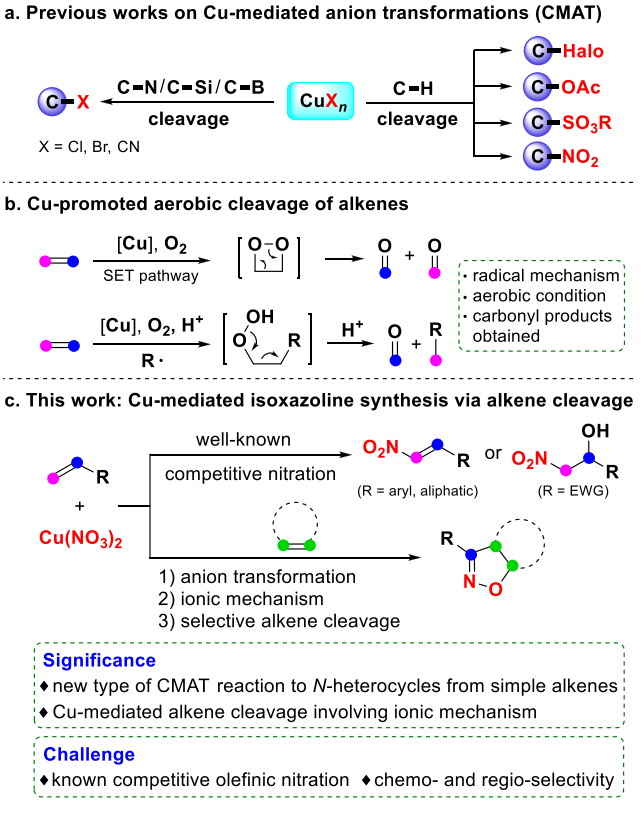
ABSTRACT: An unprecedented copper-mediated anion transformation is reported, along with selective C=C double bond cleavage and dipolar cycloaddition reaction from simple alkenes and inexpensive copper nitrate. Various transformations demonstrate the generality of this method. Further mechanistic investigation indicates a novel ionic pathway for alkene cleavage and highlights the coeffect of iodide and boric acid as additives on the inhibition of well-documented competitive nitration byproducts.



Copper-promoted coupling reaction is one of the most powerful tools in organic synthesis. In the past decades, this strategy has been widely applied in the formation and cleavage of inert chemical bonds, leading to complicated molecules or heterocyclic compounds.[1] For example, the Chan−Evans−Lam coupling reaction is a frequently used method for C−N bond formation,[2] while the Ullmann reaction provides an efficient pathway to biaryls through C−C bond formation.[3] The characteristics of low cost and abundant reserves make copper salts favorable over other noble transition metals and acceptable to use in stoichiometric amounts in reactions. Thus, more and more attention has been given to copper-mediated anion transformations. In these reactions, copper salt acts not only as a reagent, but also as a crucial promoter or catalyst (Scheme 1a). The classic Sandmeyer reaction is representative, involving C−X (X = Cl, Br, CN) bond formation through C−N bond cleavage.[4] Alternatively, C−Si[5] and C−B[6] bond functionalization were further explored with stoichiometric copper salts. In recent decades, copper-mediated anion transformations involving C−H functionalization turn out to be a superior choice. An elegant example was reported by Yu group, where $Cu(OAc)_2$ was employed for acetylation and hydroxylation.[7] Almost at the same time, Shi and co-workers developed a *ortho* C−H chlorination in the presence of $CuCl_2$.[8] Isocyanide induced activation of copper sulfate is recently disclosed by our group, affording sulfonic esters through C−H sulfonation.[9] Besides, copper nitrate has been proven to be a common and versatile reagent[10] for the synthesis of nitro compounds,[11] nitrates,[12] and heterocycles.[13]

Transition-metal-promoted alkene cleavage is a fundamental functional group interconversion in olefin chemistry, and takes a privileged position in the synthesis of a wide variety of natural products, pharmaceuticals, and functional materials.[14] Oxidative cleavage using Lemieux−Johnson protocol[15] and

Scheme 1. Copper-Mediated Anion Transformations and Alkene Cleavage



Received: August 4, 2019

DOI: 10.1021/acs.orglett.9b02748
Org. Lett. XXXX, XXX, XXX−XXX

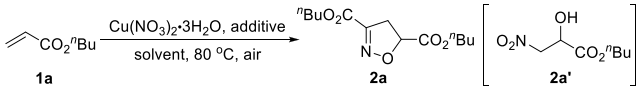
ring-closing metathesis (RCM) process[16] are two of the most common methods, although noble metals and toxic reagents are often required. Recently, great progresses have been made on copper-promoted aerobic alkene cleavage (Scheme 1b).[17] However, in most cases, only carbonyl products are generally obtained via radical pathway with the assistance of copper salts and oxygen. Herein, we report an unprecedented copper nitrate-mediated anion transformation from simple alkenes to isoxazolines, involving sequential one C=C double bond cleavage and three new chemical bond formations (Scheme 1c). The significance of this given chemistry is 3-fold: (1) it is the first example for the synthesis of N-heterocycles through the combination of copper-mediated anion transformation and selective alkene cleavage; (2) easily accessible nitroalkenes[18] and nitroethanols,[19] by well-documented olefinic competitive nitration reaction, are greatly inhibited through the coeffect of iodide and boric acid as additives; and (3) different from the previous works, copper-mediated selective alkene cleavage is realized in this work through a novel ionic pathway.

We commenced the study by examining the reaction of *n*-butyl acrylate (**1a**) with copper nitrate trihydrate in acetonitrile. Intriguingly, the desired isoxazoline product **2a** was afforded in 33% yield, along with the unexpected formation of **2a′** in 27% yield (Table 1, entry 1). Other solvents including toluene, dioxane, DMSO, EtOH, and PhCN were proven to be less efficient in this reaction (Table 1, entries 2–6). A further screening of various nitrate salts indicated that copper nitrate was crucial to the success of this transformation, since ferric, cobalt, or potassium nitrate failed to initiate the reaction (Table 1, entry 7). Surprisingly, the yield of **2a** increased dramatically to 53% when 1 equiv of NaI was employed as an additive (Table 1, entry 8). This result encouraged us to examine a series of additives, and KI was the best choice since the undesired byproduct **2a′** was almost inhibited under the conditions (Table 1, entries 9–12). To our delight, desired product could be isolated in 80% yield when mixed solvent was used (Table 1, entry 13), and the yield of **2a** increased to 87% in the presence of 1 equiv of boric acid (Table 1, entry 14).[20] After further optimization of solvent ratio, temperature, and atmosphere, we confirmed that the reaction performed best at 80 °C under an air atmosphere (Table 1, entry 14 vs entries 15–21).

With the optimized reaction conditions in hand, we next examined the substrate scope of alkenes (Scheme 2). Various acrylates performed smoothly (**2a–2f**), albeit a slightly decreased yield was obtained for the sterically hindered substrate (**2f**). Success of this transformation could also be applied to vinyl ketones, regardless of aryl or aliphatic substituents (**2g–2k**). Furthermore, the reaction conditions were also suitable for acrylamides (**2l** and **2m**). However, no corresponding product could be generated from acrylonitrile substrate (**2n**), which might be due to the strong coordination of the cyano group to the Cu center.

Generally, it is relatively more difficult to realize the intermolecular reactions for alkene substrates in a chemoselective manner, compared with intramolecular ones. The difficulty lies in promoting the desired reaction selectively while avoiding the unexpected homocoupling reactions.[21] We contemplated the problem might be overcome through increasing the amount of copper nitrate, so that the alkene substrate with slightly higher reactivity will be quickly turned

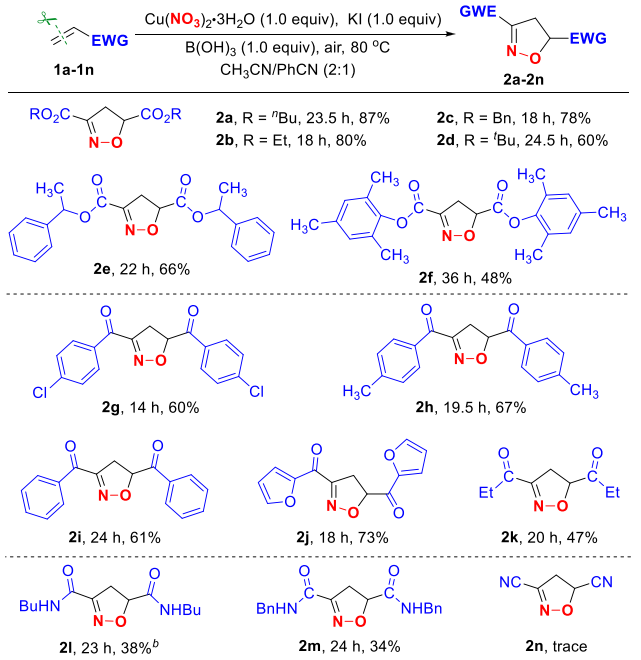
Table 1. Optimization of Reaction Conditions[a]



entry	solvent	additive	yield[b] (%)
1	CH_3CN	/	33 (27)
2	toluene	/	<5
3	dioxane	/	20
4	DMSO	/	<5
5	EtOH	/	<5
6	PhCN	/	16
7	CH_3CN	/	<5[c]
8	CH_3CN	NaI	53
9	CH_3CN	KI	66
10	CH_3CN	TBAI	29
11	CH_3CN	LiI·H_2O	58
12	CH_3CN	KBr	<5
13	CH_3CN/PhCN (2:1)	KI	80
14	CH_3CN/PhCN (2:1)	**KI + B(OH)$_3$**	**87**
15	CH_3CN/PhCN (1:1)	KI + B(OH)$_3$	74
16	CH_3CN/PhCN (5:1)	KI + B(OH)$_3$	75
17	CH_3CN/PhCN (1:2)	KI + B(OH)$_3$	72
18	CH_3CN/PhCN (2:1)	KI + B(OH)$_3$	77[d]
19	CH_3CN/PhCN (2:1)	KI + B(OH)$_3$	82[e]
20	CH_3CN/PhCN (2:1)	KI + B(OH)$_3$	73[f]
21	CH_3CN/PhCN (2:1)	KI + B(OH)$_3$	78[g]

[a]Reaction conditions: **1a** (0.4 mmol), $Cu(NO_3)_2·3H_2O$ (0.4 mmol), additive (0.4–0.8 mmol), solvent (2.0 mL), air, 80 °C, 18–20 h. [b]Isolated yield of product **2a**. Yield of byproduct **2a′** is given in the parentheses. [c]$Fe(NO_3)_3·9H_2O$, $Co(NO_3)_2·6H_2O$ or KNO_3 was used as nitrogen source instead of $Cu(NO_3)_2·3H_2O$. [d]At 70 °C. [e]At 90 °C. [f]Under O_2. [g]Under N_2.

Scheme 2. Substrate Scope of Alkenes[a]

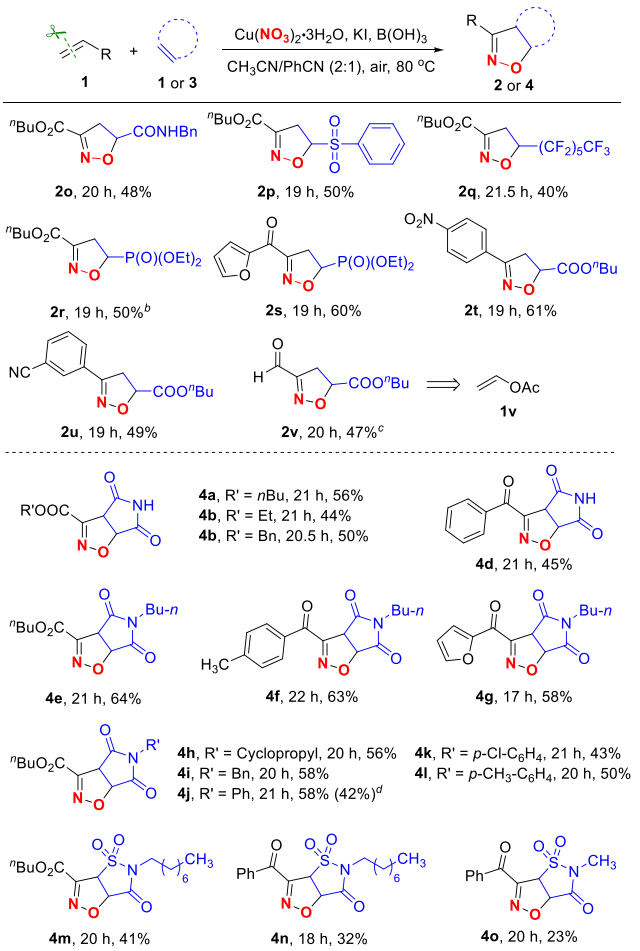


[a]Reaction conditions: **1** (0.4 mmol), $Cu(NO_3)_2·3H_2O$ (1.0 equiv), KI (1.0 equiv), $B(OH)_3$ (1.0 equiv), CH_3CN/PhCN (2:1, v/v, 2.0 mL), air, 80 °C. Yields shown are of the isolated products. [b]The reaction was performed in CH_3CN.

DOI: 10.1021/acs.orglett.9b02748
Org. Lett. XXXX, XXX, XXX–XXX

into the intermediate, and then captured by another alkene. Acrylates and vinyl ketones were then chosen as the substrates for the modular synthesis, which afforded isoxazolines selectively with various substituents at 3- and 5-positions, as shown in Scheme 3. The reaction features good functional

Scheme 3. Substrate Scope of Alkenes for Intermolecular Reactions[a]



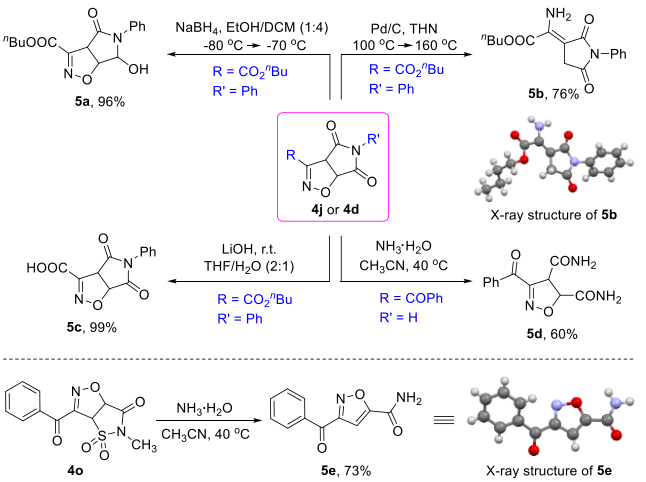
[a]Reaction conditions: **1** (0.3 mmol), **1** or **3** (4.0 equiv), $Cu(NO_3)_2 \cdot 3H_2O$ (4.0 equiv), KI (1.0 equiv), $B(OH)_3$ (1.0–2.0 equiv), CH_3CN/PhCN (2:1, v/v, 3.0 mL), air, 80 °C. Yields shown are of the isolated products. [b]In CH_3CN. [c]At 70 °C. [d]The reaction was conducted in 1 g scale.

group tolerance, for example, amide (**2o**), sulfonyl (**2p**), perfluoroalkyl (**2q**), and phosphate (**2r** and **2s**) substituents could be successfully assembled on the isoxazoline skeleton using this method without exception. Surprisingly, cleavage of the C=C double bond occurred selectively on styrene substrates (**1t** and **1u**) rather than acrylate **1a**, leading to 3-aryl substituted isoxazolines **2t** and **2u**, respectively. The reason could be ascribed to the stronger electron-withdrawing property of styrene containing nitro or cyano group, compared with acrylate. When vinyl acetate **1v** was treated with acrylate **1a**, 3-formyl isoxazoline **2v** was isolated as a major product. In this reaction, we speculated that copper nitrate might be inclined to coordinate with the electron-rich C=C double bond of **1v**, generating β-nitro hemiacetal as key intermediate. For the reaction of ethyl acrylate and phenylacetylene, 3-benzoyl isoxazoline and isoxazole were afforded by initiating the reaction from alkyne instead of acrylate.[13a]

To further demonstrate the generality of this reaction, a variety of cyclic alkenes were explored as the dipolarophiles. Pleasingly, the fused bicyclic products were afforded for both acrylates (**4a–4c**) and vinyl ketone (**4d**) with free N–H untouched. Alternatively, N-substituted maleimides could also act as good dipolarophiles in the cycloaddition, regardless of aliphatic or aryl substituents on the nitrogen atom (**4e–4l**). Notably high regioselectivity was obtained during the cycloaddition, affording products (**4m–4o**) without regio-isomers. After oxidative aromatization, the obtained "saccharin-like" compounds could be further converted into structural analogues of commercial nonsteroidal anti-inflammatory drugs (NSAID) Tenoxicam and Piroxicam.[22]

To illustrate the utility of this approach, further transformations of generated products were performed (Scheme 4).

Scheme 4. Transformations of Products

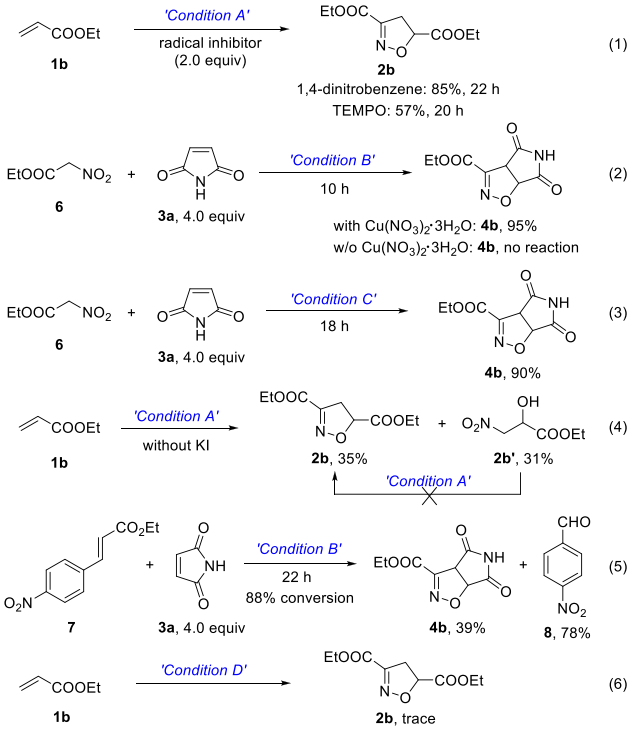


Because of the inductive effect of oxygen atom in isoxazoline ring, the carbonyl group at its β-position could be reduced selectively at low temperature in the presence of $NaBH_4$,[23] affording the lactam product **5a** in excellent yield. Alternatively, under the reductive conditions of Pd/C and tetrahydronaphthalene (THN), product **5b** was obtained in 76% yield with the isoxazoline ring broken, the structure of which was further determined by X-ray diffraction.[24] Note that no approach has been documented to prepare the amino acid-derived polysubstituted captodative alkenes so far. As expected, the alkoxy carbonyl group on the 3-position could smoothly be hydrolyzed into the carboxylic group almost quantitatively under mild basic conditions (**5c**). When ammonium hydroxide was used as the base, fully substituted isoxazoline **5d** was achieved in 60% yield, which was hard to synthesize through other approaches. However, under the same conditions, aromatized isoxazole **5e** was obtained from **4o**, where the sulfonyl group was eliminated during the reaction.[24]

To define the possible intermediate and clarify the pathway of the reaction, a series of control experiments were conducted (Scheme 5). The reaction occurred smoothly in the presence of radical inhibitors such as 1,4-dinitrobenzene or 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO), which suggested that the radical mechanism might be ruled out (eq 1 in Scheme 5). Based on the fact that ethyl-2-nitroacetate **6** could be transformed to the final product in almost quantitative yield,

DOI: 10.1021/acs.orglett.9b02748
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 5. Preliminary Mechanistic Studies

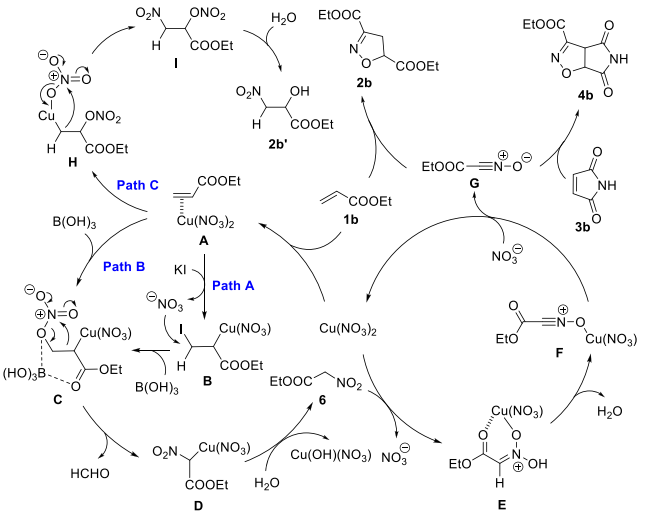


Condition A: $Cu(NO_3)_2{\cdot}3H_2O$ (1.0 equiv), KI (1.0 equiv), $B(OH)_3$ (1.0 equiv) CH_3CN/PhCN (2:1), 80 °C, air.
Condition B: $Cu(NO_3)_2{\cdot}3H_2O$ (4.0 equiv), KI (1.0 equiv), $B(OH)_3$ (2.0 equiv) CH_3CN/PhCN (2:1), 80 °C, air.
Condition C: $Cu(NO_3)_2{\cdot}3H_2O$ (30 mol%), CH_3CN/PhCN (2:1), 80 °C, air.
Condition D: CuI (1.0 equiv), KNO_3 (2.0 equiv), I_2 (0.5 equiv), $B(OH)_3$ (1.0 equiv) CH_3CN/PhCN (2:1), 80 °C, air.

we speculated that the nitro compound **6** might be the key intermediate during the reaction (eq 2 in Scheme 5). No product could be isolated in the absence of copper salt, while a reasonable yield was obtained in the presence of 30 mol % of copper salt (eq 3 in Scheme 5), which indicated that copper nitrate was crucial and acted as a catalyst for the cycloaddition process. When the reaction was conducted in the absence of KI, the desired product **2b** and byproduct **2b′** was isolated in 35% and 31% yield, respectively. Considering **2b′** was not observed under standard conditions and failed to convert into **2b** (eq 4 in Scheme 5), KI was proposed to play a significant role in the selective synthesis of products. To our delight, 4-nitrobenzaldehyde **8** was isolated in 78% yield when (*E*)-ethyl 3-(4-nitrophenyl)acrylate **7** was used as the substrate, which suggested that the formed aldehyde was the leaving fragment after cleavage of the C═C double bond (eq 5 in Scheme 5). Based on the documented result that copper nitrate would be transformed to CuI and iodine in the presence of iodide,[25] to illustrate the reaction intermediate, we next conducted the reaction with CuI, I_2, and KNO_3, instead of $Cu(NO_3)_2{\cdot}3H_2O$ and KI. However, a trace amount of product **2b** was observed, which will exclude CuI or I_2 as the intermediate during the reaction (eq 6 in Scheme 5).

Although a detailed reaction pathway remains to be clarified, a plausible mechanism for this reaction was proposed on the basis of the above results (Scheme 6). Initially, copper nitrate was coordinated with the C═C double bond to give complex **A**, then complex **B** was generated from **A** with the assistance of KI (Path A). The nucleophilic substitution of nitrate anion occurred to afford complex **C** in the presence of boric acid,

Scheme 6. Plausible Mechanism



which may also be achieved directly via the insertion reaction in complex **A** (Path B). After an intramolecular rearrangement and successive hydrolysis, the key intermediate **6** would be formed with the exclusion of formaldehyde. In this step, boric acid might be coordinated with the O atoms in ester and nitrate groups,[20] which will further assist the C−C bond cleavage. Subsequently, nitro compound **6** would be activated by copper nitrate.[13] After the isomerization and dehydrating process, the free nitrate anion assisted the cleavage of the O−Cu bond in complex **F**, which could be further transformed to the nitrile oxide **G**.[26] The final products **2b** and **4b** would be obtained from **G**, respectively, through the well-documented [3 + 2] cycloaddition of nitrile oxide and alkene. On the other hand, under the circumstance without KI, the bulky Cu atom was assembled on the less-hindered carbon of alkene and generated complex **H**. The byproduct **2b′** was then formed through successive rearrangement and hydrolysis process[19] (Path C). Presumably, the coeffect of KI and boric acid will make Paths A and B more dominant than Path C.

In conclusion, we have disclosed a novel copper nitrate-mediated anion transformation from simple alkenes via selective alkene cleavage and successive dipolar cycloaddition reaction, affording pharmacologically interesting isoxazoline skeletons in excellent regioselectivity and chemoselectivity. The overall conversion involves a sequence of one C═C double bond cleavage and the formation of three new chemical bonds. The good selectivity and various transformations of given products could be highlighted on the promising prospect of the present method, leading to newly built skeletons in diversity. Further mechanistic investigation provides a distinguishing ionic pathway and indicates the coeffect of iodide and boric acid as additives on the inhibition of well-documented competitive nitration reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02748.

Experimental procedures and characterization data for all compounds (PDF)

DOI: 10.1021/acs.orglett.9b02748
Org. Lett. XXXX, XXX, XXX−XXX

Accession Codes

CCDC 1895015−1895016 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xubin@shu.edu.cn.

ORCID

Mingchun Gao: 0000-0002-8564-4387
Bin Xu: 0000-0002-9251-6930

Author Contributions

§These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Nos. 21871174 and 21672136) and Innovation Program of Shanghai Municipal Education Commission (No. 2019-01-07-00-09-E00008) for financial support. The authors thank Prof. Qitao Tan (SHU), Prof. Changhua Ding (SHU), and Prof. Ming-Hua Xu (SUSTech) for helpful discussion; Prof. Bingxin Liu (SHU) for analysis of single-crystal X-ray diffraction; and Prof. Hongmei Deng (SHU) for NMR spectroscopic measurements.

REFERENCES

(1) For recent reviews on isocyanides, see: (a) McCann, S. D.; Stahl, S. S. *Acc. Chem. Res.* **2015**, *48*, 1756. (b) Guo, X.-X.; Gu, D.-W.; Wu, Z.; Zhang, W. *Chem. Rev.* **2015**, *115*, 1622. (c) Thapa, S.; Shrestha, B.; Gurung, S. K.; Giri, R. *Org. Biomol. Chem.* **2015**, *13*, 4816. (d) Liu, J.; Chen, G.; Tan, Z. *Adv. Synth. Catal.* **2016**, *358*, 1174. (e) Jadhav, A. P.; Ray, D.; Rao, V. U. B.; Singh, R. P. *Eur. J. Org. Chem.* **2016**, *2016*, 2369. (f) Zhu, X.; Chiba, S. *Chem. Soc. Rev.* **2016**, *45*, 4504.

(2) (a) Chan, D. M. T.; Monaco, K. L.; Wang, R.-P.; Winters, M. P. *Tetrahedron Lett.* **1998**, *39*, 2933. (b) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937. (c) Lam, P. Y. S.; Clark, C. G.; Saubern, S.; Adams, J.; Winters, M. P.; Chan, D. M. T.; Combs, A. *Tetrahedron Lett.* **1998**, *39*, 2941.

(3) Ullmann, F.; Bielecki, J. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2174.

(4) Sandmeyer, T. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 2650.

(5) For selected examples, see: (a) Lökös, M.; Hegyes, P.; Földeák, S. *J. Organomet. Chem.* **1984**, *275*, 27. (b) Tamao, K.; Akita, M.; Kato, H.; Kumada, M. *J. Organomet. Chem.* **1988**, *341*, 165. (c) Zhu, J.; Wang, F.; Huang, W.; Zhao, Y.; Ye, W.; Hu, J. *Synlett* **2011**, *2011*, 899.

(6) For selected examples, see: (a) Masuda, Y.; Hoshi, M.; Arase, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2725. (b) Masuda, Y.; Suyama, T.; Murata, M.; Watanabe, S. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2955. (c) Thompson, A. L. S.; Kabalka, G. W.; Akula, M. R.; Huffman, J. W. *Synthesis* **2005**, *2005*, 547. (d) Murphy, J. M.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 15434.

(7) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790.

(8) Wan, X.; Ma, Z.; Li, B.; Zhang, K.; Cao, S.; Zhang, S.; Shi, Z. *J. Am. Chem. Soc.* **2006**, *128*, 7416.

(9) Hong, X.; Tan, Q.; Liu, B.; Xu, B. *Angew. Chem., Int. Ed.* **2017**, *56*, 3961.

(10) Gao, M.; Ye, R.; Shen, W.; Xu, B. *Org. Biomol. Chem.* **2018**, *16*, 2602.

(11) For selected examples, see: (a) Fan, Z.; Ni, J.; Zhang, A. *J. Am. Chem. Soc.* **2016**, *138*, 8470. (b) Gao, M.; Xu, B. *Org. Lett.* **2016**, *18*, 4746. (c) Zhang, Y.; Dan, W.; Fang, X. *Organometallics* **2017**, *36*, 1677. (d) Bose, A.; Mal, P. *Chem. Commun.* **2017**, *53*, 11368.

(12) Gao, M.; Zhou, K.; Xu, B. *Adv. Synth. Catal.* **2019**, *361*, 2031.

(13) For selected examples, see: (a) Gao, M.; Li, Y.; Gan, Y.; Xu, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 8795. (b) Li, Y.; Gao, M.; Liu, B.; Xu, B. *Org. Chem. Front.* **2017**, *4*, 445. (c) Lin, Y.; Zhang, K.; Gao, M.; Jiang, Z.; Liu, J.; Ma, Y.; Wang, H.; Tan, Q.; Xiao, J.; Xu, B. *Org. Biomol. Chem.* **2019**, *17*, 5509.

(14) For reviews on alkene cleavage, see: (a) Bidange, J.; Fischmeister, C.; Bruneau, C. *Chem. - Eur. J.* **2016**, *22*, 12226. (b) Wang, T.; Jiao, N. *Acc. Chem. Res.* **2014**, *47*, 1137. (c) Spannring, P.; Bruijnincx, P. C. A.; Weckhuysen, B. M.; Klein Gebbink, R. J. M. *Catal. Sci. Technol.* **2014**, *4*, 2182.

(15) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, *21*, 478.

(16) Grubbs, R. H.; Trnka, T. M. In *Ruthenium in Organic Synthesis*; Murahashi, S., Ed.; Wiley−VCH: Weinheim, Germany, 2005; pp 153−178.

(17) For selected examples, see: (a) Tokunaga, M.; Shirogane, Y.; Aoyama, H.; Obora, Y.; Tsuji, Y. *J. Organomet. Chem.* **2005**, *690*, 5378. (b) Liu, D.; Yu, J.; Cheng, J. *Tetrahedron* **2014**, *70*, 1149. (c) Zhou, Y.; Rao, C.; Mai, S.; Song, Q. *J. Org. Chem.* **2016**, *81*, 2027. (d) Lippincott, D. J.; Trejo-Soto, P. J.; Gallou, F.; Lipshutz, B. H. *Org. Lett.* **2018**, *20*, 5094.

(18) Naveen, T.; Maity, S.; Sharma, U.; Maiti, D. *J. Org. Chem.* **2013**, *78*, 5949.

(19) Jayakanthan, K.; Madhusudanan, K. P.; Vankar, Y. D. *Tetrahedron* **2004**, *60*, 397.

(20) For a review, see: (a) Pal, R. *ARKIVOC* **2018**, 346. For selected examples, see: (b) Sravan Kumar, J.; Jonnalagadda, S. C.; Mereddy, V. R. *Tetrahedron Lett.* **2010**, *51*, 779. (c) Garimallaprabhakaran, A.; Harmata, M. *Synlett* **2011**, *2011*, 361. (d) Xiang, J.-C.; Cheng, Y.; Wang, M.; Wu, Y.-D.; Wu, A.-X. *Org. Lett.* **2016**, *18*, 4360. (e) Vantourout, J. C.; Miras, H. N.; Isidro-Llobet, A.; Sproules, S.; Watson, A. J. B. *J. Am. Chem. Soc.* **2017**, *139*, 4769. (f) Tian, M.; Bai, D.; Zheng, G.; Chang, J.; Li, X. *J. Am. Chem. Soc.* **2019**, *141*, 9527.

(21) (a) Hatamoto, Y.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **2004**, *6*, 4623. (b) Xu, Y.-H.; Lu, J.; Loh, T.-P. *J. Am. Chem. Soc.* **2009**, *131*, 1372. (c) Yu, H.; Jin, W.; Sun, C.; Chen, J.; Du, W.; He, S.; Yu, Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 5792. (d) Wen, Z.-K.; Xu, Y.-H.; Loh, T.-P. *Chem. - Eur. J.* **2012**, *18*, 13284.

(22) Burri, K. F. *Helv. Chim. Acta* **1989**, *72*, 1416.

(23) Stepakov, A. V.; Ledovskaya, M. S.; Boitsov, V. M.; Molchanov, A. P.; Kostikov, R. R.; Gurzhiy, V. V.; Starova, G. L. *Tetrahedron Lett.* **2012**, *53*, 5414.

(24) For crystallographic data of compound **5b** and **5e**, see the Supporting Information.

(25) Frouzanfar, H.; Kerridge, D. H. *J. Inorg. Nucl. Chem.* **1979**, *41*, 181.

(26) Campbell, M. M.; Cosford, N. D. P.; Rae, D. R.; Sainsbury, M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 765.

DOI: 10.1021/acs.orglett.9b02748
Org. Lett. XXXX, XXX, XXX−XXX