Published in final edited form as:

Chemistry. 2014 October 20; 20(43): 13901–13904. doi:10.1002/chem.201404381.

Cu(I)-Catalyzed Sequential Diamination and Dehydrogenation of Terminal Olefins: A Facile Approach to Imidazolinones

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Abstract

Diamination of olefins presents a powerful strategy to access vicinal diamines. During the last decade, metal-catalyzed diamination of olefins has received considerable attention. This paper describes an efficient sequential diamination and dehydrogenation process of terminal olefins with CuBr as catalyst and di-*tert*-butyldiaziridinone as nitrogen source, providing a facile and viable approach to a variety of imidazolin-2-ones, which are important structural motifs present in various biologically active molecules.

Keywords

diamination; dehydrogenation; diaziridinone; copper catalysts; imidazolinones

Diamination of olefins provides a straightforward approach to vicinal diamines, which are contained in a variety of biologically and chemically significant molecules.^[1] A number of effective metal-mediated^[2,3] and metal-catalyzed^[3c,4–10] diamination processes have been reported. In our own studies, we have developed Pd(0)^[11,12] and Cu(I)-catalyzed^[13] diaminations of olefins using di-*tert*-butyldiaziridinone (**1**)^[14] as nitrogen source. When terminal olefin **2** was used as substrate, the diamination with Pd(0) and diaziridinone **1** occurred at allylic and homoallylic carbons (Scheme 1).^[12] This process likely proceeded via dehydrogenation of the terminal olefin to form diene intermediate **3**, which was subsequently diaminated in situ to give product **4**.^[12] In our continuing efforts to explore the reactivity of diaziridinone and expand its synthetic utility, we have found that imidazolin-2-one **7** can be obtained when terminal olefin **5** was treated with di-*tert*-butyldiaziridinone (**1**) and CuBr, likely via a sequential diamination and dehydrogenation process (Scheme 1). Imidazolin-2-ones are important functional moieties present in various biologically active compounds,^[15] such as dopamine D₄ receptor antagonist,^[15a] antibacterial MurB inhibitors,^[15b] CGRP receptor antagonist,^[15d] and antitumor agents^[15g] (Figure 1). Imidazolin-2-ones can generally be synthesized by the cyclization of α -amino carbonyl compounds, propargylic ureas, and related compounds,^[15,16] or by further derivatization of imidazolin-2-ones.^[17] Herein we wish to report our preliminary studies on the Cu(I)-catalyzed sequential diamination and dehydrogenation process of terminal olefins.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201xxxxx>.

Our initial diamination studies were carried out with styrene (**5a**) as test substrate and di-*tert*-butyldiaziridinone (**1**) as nitrogen source under various conditions. As shown in Table 1, no reaction was observed in many cases (Table 1, entries 1–7). However, when styrene was treated with 10 mol% CuCl and 3.5 equiv of di-*tert*-butyldiaziridinone (**1**) in CH₃CN at rt for 9 h, imidazolin-2-one **7a**, instead of diamination product **6a**, was formed as major product and isolated in 59% yield (Table 1, entry 8) (the X-ray structure of **7a** is shown in Figure 2). The formation of **7a** was somewhat unexpected. A slightly higher yield (63%) was obtained for **7a** with CuBr (Table 1, entry 11), and the yield was increased to 85% via slow addition of di-*tert*-butyldiaziridinone (**1**) (Table 1, entry 12).

The diamination–dehydrogenation process can be extended to various *para*-, *meta*-, *ortho*-, and disubstituted styrenes, providing the corresponding imidazolin-2-ones in 70–91% yield (Table 2, entries 2–11). Heteroarylethenes, enone, and enyne were also effective substrates, giving imidazolin-2-ones in 51–88% yield (Table 2, entries 12–15). The method is amenable to gram scale as illustrated in the case of imidazolin-2-one **7a** (Table 2, entry 1). As demonstrated in Scheme 2, removal of *tert*-butyl group can be achieved with CF₃CO₂H and concentrated HCl. Treating **7a** with CF₃CO₂H at 65 °C for 5 h resulted in selective monodeprotection to afford compound **8a** in 98% yield. Both *tert*-butyl groups were removed in concentrated HCl at 100 °C, giving compound **9a** in 87% yield.

When the reaction was carried out with 1.0 equiv of di-*tert*-butyldiaziridinone (**1**), diamination product **6a** and imidazolin-2-one **7a** were obtained from styrene (**5a**) in 23% and 26% yields, respectively (Scheme 3, eq 1). The structure of **6a** was confirmed by the X-ray analysis (see Supporting Information). Treatment of **6a** with 1.0 equiv of diaziridinone **1** and 10 mol% CuBr in CH₃CN at rt led to imidazolin-2-one **7a** in 72% yield (Scheme 3, eq 2). These results suggest that compound **6a** is a possible reaction intermediate for **7a**.

While a precise understanding of the reaction mechanism awaits further study, a plausible catalytic cycle is proposed in Scheme 4. The CuBr first reductively cleaves the N–N bond of di-*tert*-butyldiaziridinone (**1**) to form Cu(II) nitrogen radical **A**,^[13a,f,18] which adds to terminal olefin **5** to give radical intermediate **B**. The ring closure of **B** results in compound **6** and regenerates CuBr catalyst. Compound **6** is subsequently converted into imidazolin-2-one **7** via hydrogen abstraction by radical species **A** with formation of urea and regeneration of CuBr catalyst.^[19]

In summary, we have developed a novel sequential diamination and dehydrogenation process of terminal olefins using CuBr as catalyst and di-*tert*-butyldiaziridinone (**1**) as nitrogen source. A variety of imidazolin-2-ones can be obtained in good yields under mild conditions. The reaction is also amenable to gram scale. The resulting imidazolin-2-ones can be selectively monodeprotected as well as completely deprotected. The present method provides ready access to imidazolin-2-ones, which are important functional motifs contained in biologically significant molecules. Further development of other reaction processes with diaziridinone and related compounds is currently underway.

Experimental Section

Representative Procedure for the Sequential Diamination and Dehydrogenation of Olefins (Table 2, entry 1)

A 50 mL single-necked flask charged with CuBr (0.1148 g, 0.80 mmol) was evacuated and filled with argon three times. After the addition of CH₃CN (16 mL) and styrene (**5a**) (0.8332 g, 8.0 mmol), di-*tert*-butyldiaziridinone (**1**) (4.767 g, 28.0 mmol) was slowly added via syringe pump at rt over 7 h. Upon vigorously stirring at rt for an additional 2 h, the reaction mixture was concentrated and purified by flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1 to 15:1 to 10:1) to give imidazolinone **7a** as a white solid (1.833 g, 84%).

Acknowledgments

We are grateful for the generous financial support from the General Medical Sciences of the National Institutes of Health (GM083944-07).

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Figure 1.
Imidazolinone-containing biologically active compounds.

Figure 2.
X-ray structure of imidazolin-2-one **7a**.

Scheme 1.
Diamination of terminal olefins.

Scheme 2.
Deprotection of imidazolin-2-one **7a**.

Scheme 3.

Scheme 4.
Proposed catalytic cycle.

Table 1Studies on reaction conditions.^[a]

Entry	Catalyst	Solvent	Yield [%] ^[b]
1	CuCl-P(<i>n</i> Bu) ₃ (1:1)	CHCl ₃	0
2	CuCl	CHCl ₃	0
3	CuCl	CH ₂ Cl ₂	0
4	CuCl	ClCH ₂ CH ₂ Cl	0
5	CuCl	PhH	0
6	CuCl	PhCH ₃	0
7	CuCl	THF	0
8	CuCl	CH ₃ CN	59
9	CuI	CH ₃ CN	2
10	CuCN	CH ₃ CN	12
11	CuBr	CH ₃ CN	63
12 ^[c]	CuBr	CH ₃ CN	85

^[a] All reactions were carried out with styrene (**5a**) (0.40 mmol), di-*tert*-butyldiaziridinone (**1**) (1.40 mmol) (added in one portion), and Cu(I) catalyst (0.040 mmol) in solvent (0.80 mL) at rt under argon for 9 h unless otherwise stated.

^[b] Isolated yield based on styrene.

^[c] Di-*tert*-butyldiaziridinone (**1**) was slowly added via syringe pump over 7 h, and the reaction mixture was then stirred for an additional 2 h.

Table 2CuBr-catalyzed sequential diamination and dehydrogenation of terminal olefins.^[a]

Entry	Substrate 5	Product 7	Yield [%] ^[b]
1 ^[c]	5a, X = H	7a	84
2	5b, X = <i>p</i> -F	7b	78
3	5c, X = <i>p</i> -Cl	7c	87
4	5d, X = <i>p</i> -Br	7d	85
5	5e, X = <i>p</i> -Me	7e	71
6	5f, X = <i>p</i> - <i>t</i> Bu	7f	80
7	5g, X = <i>m</i> -Cl	7g	86
8	5h, X = <i>o</i> -F	7h	84
9			88
	5i	7i	
10			91
	5j	7j	
11			70
	5k	7k	
12			88
	5l	7l

Entry	Substrate 5	Product 7	Yield [%] ^[b]
13			67
14 ^[d]			51
15 ^[d]			75

^[a] All reactions were carried out with olefin **5** (0.40 mmol), di-*tert*-butyldiaziridinone (**1**) (1.40 mmol) (added slowly via syringe pump over 7 h), and CuBr (0.040 mmol) in CH₃CN (0.80 mL) at rt under argon for 9 h unless otherwise stated.

^[b] Isolated yield.

^[c] The reaction was carried out on 8.0 mmol scale of **5a**.

^[d] Reaction time, 48 h.