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Copper-catalyzed pyrrole synthesis from 3,6-dihydro-1,2-oxazines

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Highly-functionalized pyrroles could be effectively synthesized from 3,6-dihydro-1,2-oxazines using a heterogeneous copper on carbon (Cu/C) under neat heating conditions. Furthermore, the in situ formation of 3,6-dihydro-1,2-oxazines via the hetero Diels-Alder reaction between nitroso dienophiles and 1,3-dienes and the following Cu/C-catalyzed pyrrole synthesis also provided the corresponding pyrrole derivatives in a one-pot manner.

The pyrrole nucleus is an important chemical scaffold of a wide variety of functional materials, such as biologically-active compounds, pharmaceuticals, electrical conductors, etc.¹ In particular, N-aryl pyrrole derivatives exhibit a variety of interesting biological and biomedical propeties.^{1d-1g} Therefore, the development of efficient and novel synthetic methods to construct highly-functionalized pyrrole derivatives is strongly desired. 3,6-Dihydro-1,2-oxazines (3), which are easily prepared by [4+2]-cycloaddition (Diels-Alder reaction) using nitroso dienophiles (1) and 1,3-dienes (2), can be transformed into pyrroles (4) via two-step sequences (reductive N-O bond cleavage of 3 followed by oxidative cyclization of the resulting y-amino alcohol).² Although direct transformations of **3** to **4** by photolysis were accomplished,³ furan derivatives were also produced as byproducts along with the pyrroles. 6-Silyl⁴ and 4 or 6-carbonyl-substituted⁵ 3,6-dihydro-1,2-oxazines can be directly converted into the corresponding pyrrole derivatives via anionic intermediates under basic conditions. 3,6-Dihydro-1,2-oxazines bearing the 6-hydroxyl or alkoxy group (acetal derivatives) were directly transformed into pyrroles via cation intermediates using Lewis acids,⁶ Brønsted acids⁷ and silica gel.⁸ The transition metal-catalyzed reductive cycloaddition between nitroarenes (Ar-NO₂) and the 1,3-diene into 3,6dihydro-1,2-oxazines and the subsequent transformation to the pyrrole have been accomplished in a one-pot manner,

although drastic reaction conditions (over 10 bar and 200 °C) were required.⁹ Recently, a cascade synthesis of pyrroles via the hetero Diels-Alder reaction between 1-boronodienes and nitroso derivatives and the following ring contraction reaction accompanied by the elimination of the boryl function were also reported. $^{\rm 10}$ However, to the best of our knowledge, the heterogeneously-catalyzed direct transformation of simple 3,6-dihydro-1,2-oxazine derivatives into pyrroles has not been accomplished. The development of the environmentallybenign and cost-efficient synthetic procedure has been demanded from the viewpoints of green sustainable chemistry. Heterogeneous transition metal catalysts are frequently used in industrial synthetic processes because of their high stability, easy removal from the reaction mixture and reuse. The solvent-free reaction is also attractive to reduce waste and costs, and it simplifies the synthetic process and handling.¹¹ We now report an efficient heterogeneous copper on carbon (Cu/C)-catalyzed synthesis of highly-functionalized pyrrole derivatives (4) starting from easily-prepared 3,6-dihydro-1,2oxazines (3) under neat heating conditions (Scheme 1). Nitroso compounds (1) and 1,3-dienes (2) could be easily prepared from commercially available amines and aldehydes, respectively (The detailed synthetic process is described in ESI). Additionally, the one-pot synthesis via the hetero Diels-Alder reaction between nitroso dienophiles (1) and 1,3-dienes (2) could also be accomplished.



Scheme 1. Copper on carbon-catalyzed and solvent-free synthesis of pyrrole derivatives (4) from 3,6-dihydro-1,2-oxazines (3).

Our research group recently reported the palladium on carbon (Pd/C)-catalyzed dehydrogenation of 1,4-cyclohexadienes or cyclohexenes under aqueous conditions.¹² Although the

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⁺ Footnotes relating to the title and/or authors should appear here

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dehydrogenative oxidation of the 3,6-dihydro-1,2-oxazine derivatives into 1,2-oxazine derivatives was next examined, Nphenyl-6-phenyl-3,6-dihydro-1,2-oxazine (3aa: 0.2 mmol) was surprisingly transformed into the unexpected N-phenyl-2phenyl pyrrole (4aa) in 11% yield in water at 120 °C for 6 h (Table 1, entry 1). Encouraged by this result, the catalyst efficiency among a wide variety of heterogeneous transitionmetal catalysts (10% Pt/C, Rh/C, Ru/C, Ni/C, Ir/C, Au/C, Ag/C and Cu/C; each 5 mol%) was initially investigated (entries 2-9). Consequently, 10% Cu/C and 10% Au/C indicated a relatively good catalytic activity to produce 4aa, although 3aa was not completely consumed (entries 7 and 9). 4aa was never obtained without the catalyst, and **3aa** was quantitatively recovered (entry 10). On the other hand, the 10% Cu/Ccatalyzed reaction under solvent-free conditions efficiently proceeded to provide 4aa in 84% isolated yield (entries 11), while Au/C was inefficient under the neat conditions (entry 12). Additionally, the desired reaction could be hardly accomplished in organic solvents (MeCN, DMF and toluene) (entries 13-15).

Table 1. Catalyst and solvent effects.				
	Ph O N Ph 3aa (0.2 mmol)	catalyst (5 mol%) solvent (1 mL) 120 °C, 6 h	Ph Ph Ph 4aa	
entry	catalyst	solvent	yield [%] ^a	
			recovered 3aa	4aa
1	10% Pd/C	H ₂ O	39	11
2	10% Pt/C	H ₂ O	86	4
3	10% Rh/C	H ₂ O	86	2
4	10% Ru/C	H ₂ O	81	2
5	10% Ni/C	H ₂ O	91	1
6	10% lr/C	H ₂ O	90	2
7	10% Au/C	H ₂ O	44	23
8	10% Ag/C	H ₂ O	78	3
9	10% Cu/C	H ₂ O	54	27
10	_	H ₂ O	99	0
11	10% Cu/C	—	0	90 (84) ^b
12	10% Au/C	—	40	22
13	10% Cu/C	MeCN	99	0
14	10% Cu/C	DMF	66	9
15	10% Cu/C	toluene	62	38
^a Determined by ¹ H NMR using 1,4-dioxane as an internal standard. ^b Isolated yield.				

While N-penyl-2-p by the use of 10% °C (Table 1, entry 11: Table 2, entry 1), other copper species (Cu powder, CuBr and CuBr₂) indicted lower catalyst activities (entries 2-4). Lowering the reaction temperature to 100 °C and 80 °C significantly decreased the reaction efficiency (entries 1 vs. 5 and 6). Furthermore, the yield of 4aa obviously decreased when using 1 mmol of 10% Cu/C (entries 1 vs. 7) or shortening the reaction time (3 h) (entries 1 vs. 8) The present transformation could proceed under Ar and N₂ atmosphere

(entries 1 and 9), while the reaction under air led the lower yield (entry 10). The scale-up reaction using 5 mmol of 3aa could also be successfully performed to give 4aa in 72% yield (entry 11). 10% Cu/C could be reused at least fifth times without any significant loss of its catalytic activity (entries 12-15).

Table 2. Copper species and reaction temperature effects.

	Ph		Dh	
	o	catalyst (5 mol%	%) Pn	\
	Ph ⁻ N ⁻	temp., 6 h	 ₽h´ ^Ń √∕	/
	3aa		4aa	
	(0.2 mmol)	-	-	
entry	catalyst	temp. [°C]	yield [%] ^a	
			recovered	4aa
			3aa	
1	10% Cu/C	120	0	90 (84) ^b
2	Cu (0) powder	120	39	45
3	CuBr	120	0	56
4	CuBr ₂	120	0	32
5	10% Cu/C	100	69	26
6	10% Cu/C	80	100	0
7 ^c	10% Cu/C	120	0	79
8 ^d	10% Cu/C	120	20	62
9 ^e	10% Cu/C	120	0	85
10 ^{<i>f</i>}	10% Cu/C	120	33	40
11^g	10% Cu/C	120	0	72 ^b
12 ^{<i>h,i</i>}	10% Cu/C	120	0	83
13 ^{<i>h,j</i>}	10% Cu/C	120	1	78
14 ^{<i>h,k</i>}	10% Cu/C	120	4	76
15 ^{<i>h,l</i>}	10% Cu/C	120	4	72

^a Determined by ¹H NMR using 1,4-dioxane as an internal standard. ^b Isolated yield. ^c 1 mol% of 10% Cu/C was used. ^d For 3 h. ^e Under Air. ^f Under N₂. ^g 5 mmol of 3aa was used. ^h 10% Cu/C was reused after simple filtration, washed with H₂O and MeOH, and dried in vacuo. In each run, 99, 99, 91, 93 and 93% of the Cu/C could be recovered, respectively. ¹ The second use of 10% Cu/C after the reaction in entry 1. ¹ The third use of 10% Cu/C after the reaction in entry 12. ^k The fourth use of 10% Cu/C after the eaction in entry 13. ¹ The fourth use of 10% Cu/C after the reaction in entry 14.

The scope of substrates was next investigated (Table 3). /arious N-phenyl-3-aryl-3,6-dihydro-1,2-oxazines (3ab-3ah) pearing electron-donating or electron-withdrawing groups at he para-, meta-, or ortho-position of the aromatic nucleus vere efficiently transformed into the desired pyrroles (4ablah) in good to excellent yields (entries 1-7). The furyl, thienyl or benzyl (Bn)-substituted 3,6-dihydro-1,2-oxazines (3ai-3ak) could be also converted into the corresponding pyrroles (4ailak) in good to excellent yields (entries 8-10). The reaction conditions also permitted to synthesize the trisubstituted oyrroles (4al-4ao) (entries 11-14). Various N-aryl pyrroles (4ba-4be) derived from nitrosoarene derivatives as pre-substrates (1: Scheme 1) were also effectively constructed in good yields (entries 15-18). Furthermore, the N-benzyl-3,6-dihydro-1,2oxazine derivative (3fa) was transformed into the corresponding N-benzyl pyrrole (4fa) in a moderate yield (entry 19).

	H ₂ O	44	23	re
	H₂O	78	3	
	H₂O	54	27	Т
	H₂O	99	0	٧
	_	0	90 (84) ^b	b
	_	40	22	t
	MeCN	99	0	v
	DMF	66	9	4
	toluene	62	38	C
using 1,4-dioxane as an internal standard. ^b Isolated yield.				
				4
henyl pyrr	ole (4aa) wa	s effectively	y obtained	С
Cu/C (5 mol%) under neat conditions at 120				

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Table 3. Scope of substrate.					
	substrate	10% Cu/C (5 mol%)	product		
	(3)	120 °C, 6 h	(4)		
entry	Substr	ate (3)	product (4)		
		R ¹	D 1		
	ç				
	Ph [_] N		_{Ph} ∕Ń√∕		
1	3ab : R ¹ = 4-	MeO-C ₆ H ₄	4ab: 72%		
2 ^{<i>a</i>}	3ac : R ¹ = 4-	$NO_2 - C_6 H_4$	4ac : 77%		
3	3ad : R ¹ = 4-	Br-C ₆ H ₄	4ad : 79%		
4	3ae : R ¹ = 3-	MeO-C ₆ H ₄	4ae : 67%		
5	3af : R ¹ = 3-1	Br-C ₆ H ₄	4af : 80%		
6	3ag : R ¹ = 2-	MeO-C ₆ H ₄	4ag : 61%		
7	3ah : $R^{1} = 2$ -	Br-C ₆ H ₄	4ah : 76%		
8	3ai : R ¹ = 2-1	furyl	4ai : 65%		
9	3aj : R ⁺ = 2-1	thienyl	4aj : 88%		
10	3ak : R ⁺ = Br	1	4ak : 58%		
	ľ	Br	Br Ph. /		
11	O_		M		
	Ph [_] N_	/	Ph ^{_N} _/		
	3	al	4al : 77%		
		'n	Ph		
12	٩ ٩		- Lua		
12	Ph ^{_N} _	Me	Ph ^{-N}		
	3a	m	4am : 78%		
		Ph 	Dh		
	Ç				
13 ^{<i>b</i>}	Ph [´] Ň		Ph ^Ń		
		Ph	Ph		
	3a	in	4an : 49%		
	~	Me	Me		
14 ^b	U - N	I	Me		
	Ph [/]	Me	Ph ^r		
	3a	IO Ph	4ao : 35%		
		\downarrow	Ph		
	O N				
		\checkmark			
15	3ba : R ² = 4-	Me-C ₆ H ₄	4ba : 71%		
16	3ca : R ² = 4-	Br-C ₆ H ₄	4ca : 66%		
17 ^c	3da : R ² = 3-	Br-C ₆ H ₄	4da : 66%		
18	3ea : R ² = 2-	Br-C ₆ H ₄	4ea : 34%		
		Pn 1	Ph.		
19 ^{b,d}	Ç		\geq		
	Bn∕ N		Bn ^{_N} _//		
0 = h	31	a	4fa : 46%		
For 12 h. ° 1	15 moi% of 10% C	u/c was used. ~ 10 mol% o	T 10% Cu/C was used. " For 4	48	

The one-pot synthesis of the target molecules is an important approach to shorten and simplify the synthetic route.¹³ The two-step one-pot reaction via the hetero Diels-Alder reaction and the following above-mentioned pyrrole synthesis were next examined (Scheme 2). **1** and **2** were directly transformed into the desirable pyrrole derivative (**4**) in the presence of 10%

Cu/C (5 mol%) at 120 $^{\circ}$ C for 6 h (The detailed optimization process is described in Table S1 in ESI). Consequently, various highly-functionalized pyrroles (**4aa**, **4ab**, **4ac**, **4ba** and **4ca**) could be efficiently prepared in moderate to good yields.^{14, 15}



The *N-O* bond-cleaved substrate (5), prepared by the reduction of **3aa**, was never transformed into the corresponding pyrrole product (**4aa**) under the present reaction conditions and 87% of **5** was recovered (eq. 1). Moreover, the radical-trapping experiments were conducted. When using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), galvinoxyl or 1,1-diphenylethene as a radical scavenger, the Cu/C-catalyzed transformation of **3aa** to **4aa** proceeded and the desired **4aa** was obtained in a good yield (eq. 2).¹⁶ Therefore, the single electron transfer (radical) pathway can likely be ruled out.



A suggested reaction mechanism is shown in Scheme 3. The oxidative addition of the copper species to the *N*-*O* bond of **3aa** forms intermediate **A**,^{17,18} which undergoes the β -hydride elimination to give the intermediate **B**. The subsequent reductive elimination to the intermediate **C**, dehydrative ring closure and following isomerization produced **4aa**.



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Conclusion

We have developed an efficient and direct transformation of 3,6-dihydro-1,2-oxazines into the corresponding pyrrole derivatives in the presence of only heterogeneous Cu/C. Furthermore, the one-pot pyrrole synthesis could also be accomplished via the hetero Diels-Alder reaction between nitroso dienophiles and 1,3-dienes and the subsequent Cu/C-catalyzed pyrrole synthesis. The present method under neutral conditions using an easily-removable and reusable heterogeneous Cu/C catalyst without an additive and solvent is valuable from the viewpoint of green sustainable chemistry and provides a novel synthetic process of pyrrole derivatives.

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Conflicts of interest

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There are no conflicts to declare.

Notes and references

- (a) H. Fan, J. Peng, M. T. Hamann, J.-F. Hu, *Chem. Rev.*, 2008, 108, 264–287; (b) C. T. Walsh, S. Garneau-Tsodikova, A. R. Howard-Jones, *Nat. Prod. Rep.*, 2006, 23, 517–531; (c) S. Sadki,P. Schottland, N. Brodie, G. Sabouraud, *Chem. Soc. Rev.*, 2000, 29, 283–293; (d) M. Biava, G. C. Porretta, S. Supino, G. Sleiter, *Curr. Org. Chem.*, 2007, 11, 1092–1112; (e) F. Bellina, R. Ross, *Tetrahedron*, 2006, 62, 7213–7256; (f) M. Biava, G. C. Porretta, G. Poce, S. Supino, S. Forli, M. Rovini, A. Cappelli, F. Manetti, M. Botta, L. Sautebin, A. Rossi, C. Pergola, C. Ghelardini, E. Vivoli, F. Manetti, P. Anzellotti, P. Patrignani, M. Anzini, *J. Med. Chem.*, 2007, 50, 5403–5411; (g) S. Yu, J. Saenz, J. K. Srirangam, *J. Org. Chem.*, 2002, 67, 1699–1702.
- 2 G. Calvet, N. Blanchard, C. Kouklovsky, Synthesis, 2005, 3346–3354.
- (a) R. S. Givens, D. J. Choo, S. N. Merchant, R. P. Stitt, B. Matuszewski, *Tetrahedron Lett.*, 1982, 23, 1327–1330; (b) P. Scheiner, O. L. Chapman, J. D. Lassila, *J. Org. Chem.*, 1969, 34, 813–816; (c) H. Y. Lee, D. J. Choo, *Bull. Korean Chem. Soc.*, 1993, 14, 423–424.
- 4 P. Kefalas, D. S. Grierson, *Tetrahedron Lett.*, 1993, **34**, 3555–3558.
- 5 (a) G. Kresze, H. Braun, *Tetrahedron Lett.*, 1969, **10**, 1743–1746; (b) A. Defoin, H. Fritz, G. Geffroy, J. Streith, *Tetrahedron Lett.*, 1986, 27, 3135–3138; (c) W. J. Humenny, P. Kyriacou, K. Sapeta, A. Karadeolian, M. A. Kerr, *Angew. Chem. Int. Ed.*, 2012, **51**, 11088-11091.
- K. F. McClure, S. J. Danishefsky, J. Org. Chem., 1991, 56, 850– 853.
- 7 G.-Q. Shi, M. Schlosser, Tetrahedron, 1993, 49, 1445–1456.
- 8 G. Kresze, H. Hartner, *Justus Liebigs Ann. Chem.*, 1973, 650–658.

- (a) F. Ragaini, S. Cenini, D. Brignoli, M. Gasperini, E. Gallo, J. Org. Chem., 2003, 68, 460–466; (b) F. Ragaini, S. Cenini, E. Borsani, M. Dompe, E. Gallo, Organometallics, 2001, 20, 3390–3398; (c) K. Okuro, T. Dang, K. Khumtaveeporn, H. Alper, Tetrahedron Lett., 1996, 37, 2713–2716.
- (a) F. Tripoteau, L. Eberlin, M. A. Fox, B. Carboni, A. Whiting, *Chem. Commun.*, 2013, **49**, 5414–5416; (b) L. Eberlin, B. Carboni, A. Whiting, *J. Org. Chem.*, 2015, **80**, 6574–6583.
- 11 (a) Solvent-free Organic Synthesis, ed. K. Tanaka, 2nd edn, Wiley-VCH, Weinheim, 2008; (b) Topics Current Chemistry 254, Organic Solid State Reactions, ed. F. Toda, Springer, Berlin, 2005; (c) M. A. P. Martins, C. P. Frizzo, D. N. Moreira, L. Buriol, P. Machado, Chem. Rev., 2009, 109, 4140–4182; (d) P. J. Walsh, H. Li, C. A. de Parrodi, Chem. Rev., 2007, 107, 2503–2545; (e) R. S. Varma, Pure Appl. Chem., 2001, 73, 193–198; (f) K. Tanaka, F. Toda, Chem. Rev., 2000, 100, 1025–1074.
- 12 N. Yasukawa, H. Yokoyama, M. Masuda, Y. Monguchi, H. Sajiki, Y. Sawama, Green Chem., 2018, 20, 1213–1217.
- (a) Y. Hayashi, *Chem. Sci.*, 2016, **7**, 866–880; (b) T. Newhouse, P. S. Baran, R. W. Hoffmann, *Chem. Soc. Rev.*, 2009, **48**, 3010–3021; (c) P. T. Anastas, M. M. Kirchhochhoff, *Acc. Chem. Res.*, 2002, **35**, 686–694.
- 14 Hetero Diels-Alder between nitrosobenzene (1a) and 1phenyl-1,3-butadiene (2a) gave 77% of 3aa (the detailed procedure and result are described in ESI), which was transformed to 4aa in 84% yield under the optimal reaction conditions (Table 1, entry 1). 4aa could be synthesized in 65% yield in 2 steps. The yield of the stepwise synthesis is similar to that of the one-pot procedure.
- 15 Although three steps one-pot reaction via the oxidation of amine using oxone, the hetero Diels-Alder reaction and the following Cu/C-catalyzed pyrrole synthesis was also examined, the desirable pyrrole product (**4aa**) was never obtained.
- 16 The use of 1.5 equiv. of TEMPO or galvinoxyl as a radical scavenger resulted in low yield (21% or 26%) of **4aa**, but the reaction was not completely inhibited. Meanwhile, the present Cu/C-catalyzed reaction using 1.1-diphenylethene (1.5 equiv.) could effectively proceed to provide **4aa** in 73% yield.
- 17 For recent selected papers for the oxidative addition of Cu spices to N-O bond, see: (a) M. J. Campbell, J. S. Johnson, Org. Lett., 2007, 9, 1521–1524; (b) S. Tobisch, Chem. Sci., 2017, 8, 4410–4423; (c) H. Zhu, Y. Shen, Q. Deng, T. Tu, Chem Chem., 2015, 51, 16573–16576; (d) Z. Ye, M. Dai, Org. Lett., 2015, 17, 2190–2193; (e) A. Faulkner, N. J. Race, J. S. Scott, J. F. Bower, Chem. Sci., 2014, 5, 2416–2421; (f) S. Zhu, N. Niljianskul, S. L. Buchwald, J. Am. Chem. Soc., 2013, 135, 15746–15749; (g) S. Yotphan, D. Beukeaw, V. Reutrakul, Tetrahedron, 2013, 69, 6627–6633.
- 18 For recent selected papers for the oxidative addition of metal spices other than copper to *N-O* bond, see: (a) W. C. Fu, B. Zheng, Q. Zhao, W. T. K. Chan, F. Y. Kwong, *Org. Lett.*, 2017, **19**, 4335–4338; (b) Q. Dai, P. Li, N. Ma, C. Hu, *Org. Lett.*, 2016, **18**, 5560–5563; (c) S. A. Shuler, G. Yin, S. B. Krause, C. M. Vesper, D. N. Watson, *J. Am. Chem. Soc.*, 2016, **138**, 13830–13833; (d) I. R. Hazelden, X. Ma, T. Langer, J. F. Bower, *Angew. Chem. Int. Ed.*, 2016, **55**, 11198-11202; (e) A. Faulkner, J. S. Scott, J. F. Bower, *J. Am. Chem. Soc.*, 2015, **137**, 7224–7230; (f) J. He, T. Shigenari, J.-Q. Yu, *Angew. Chem. Int. Ed.*, 2015, **54**, 6545-6549; (g) W. P. Hong, A. V. Iosub, S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 13664–13667.