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Palladium-catalyzed carbonylative cyclization of β -bromo- α,β -unsaturated carboxylic acids with 2,2-dimethylhydrazine leading to 1-(dimethylamino)-1*H*-pyrrole-2,5-diones

Yeon Kyu Bae and Chan Sik Cho*

β -Bromo- α,β -unsaturated carboxylic acids are carbonylatively cyclized with 2,2-dimethylhydrazine under carbon monoxide pressure in THF in the presence of a catalytic amount of a palladium catalyst along with a base to give 1-(dimethylamino)-1*H*-pyrrole-2,5-diones. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: β -bromo- α,β -unsaturated carboxylic acids; carbonylative cyclization; 2,2-dimethylhydrazine; 1-(dimethylamino)-1*H*-pyrrole-2,5-diones; palladium catalyst

Introduction

Transition metal-catalyzed carbonylation followed by cyclization (carbonylative cyclization) has been widely explored and used as a promising synthetic tool for the construction of the scaffolds of many pharmacologically and biologically active lactones and lactams.^[1–6] During the course of our ongoing studies directed towards palladium-catalyzed carbonylative cyclizations, we recently reported on the synthesis of several carbonyl-group-containing heterocycles such as furanones,^[7–9] alkyl 2,5-dihydro-5-oxofuran-2-carboxylates,^[10] hydroisoindol-1-ones,^[11] 1-aryl-1*H*-pyrrol-2(5*H*)-ones^[12] and maleic anhydrides^[13] from β -bromo- α,β -unsaturated aldehydes and their derivatives using such a carbonylative cyclization. The β -bromo- α,β -unsaturated aldehydes and their derivatives can be readily prepared from the corresponding α -methylene-containing ketones by the bromination conditions of the Vilsmeier–Haak reaction^[14,15] and subsequent transformation and used as a building block for the construction of various cyclic compounds.^[16–27] Under these circumstances, among the synthesis of carbonyl-group-containing heterocycles via such a carbonylative cyclization, β -bromo- α,β -unsaturated carboxylic acids were found to be cyclized with primary amines in the presence of a palladium catalyst under carbon monoxide pressure to afford *N*-alkylmaleimides.^[28] The present work was realized during the course of the extension of this protocol to the reaction with 2,2-dimethylhydrazine. Herein, we describe palladium-catalyzed carbonylative cyclization of β -bromo- α,β -unsaturated carboxylic acids with 2,2-dimethylhydrazine leading to 1-(dimethylamino)-1*H*-pyrrole-2,5-diones. It is known that 2-(dimethylamino)isoindolinone-1,3-dione (*N*-dimethylamino phthalimide), an analogue of 1-(dimethylamino)-1*H*-pyrrole-2,5-diones **3**, is used for the precursor for the synthesis of 3-substituted phthalimides, 4-substituted chlorophthalazines, dihydrobenzazepinediones, 2-pyrazolylbenzoic acids and 2-pyrazolylbenzohydrazides.^[29,30]

Results and Discussion

The results of several attempted carbonylative cyclizations of 2-bromocyclohex-1-enecarboxylic acid (**1a**) with 2,2-dimethylhydrazine (**2**) for the optimization of reaction conditions are listed in Table 1. Treatment of **1a** with an equimolar amount of **2** under CO (10 atm) in THF at 120 °C for 15 h in the presence of a catalytic amount of PdCl₂ and dppp (1,3-bis(diphenylphosphino)propane) along with Et₃N afforded 2-(dimethylamino)-4,5,6,7-tetrahydro-2*H*-isoindole-1,3-dione (**3a**) in 30% isolated yield (entry 1). The molar ratio of [**2**]/[**1a**] affected the yield of **3a** and the yield increased with the increase of the molar ratio up to 3 (entries 1–3). Lower carbon monoxide pressure resulted in a decreased yield of **3a** (entry 4). Performing the reaction in the absence of base under the molar ratio of [**2**]/[**1a**] = 5 resulted in a similar yield of **3a** (entry 5). Among solvents examined under the employed conditions, THF and dioxane were shown to be the solvent of choice (entries 3, 6–8). With other bases such as Na₂CO₃ and NaOAc combined with PdCl₂/dppp in MeCN, the yield of **3a** was generally lower than that when Et₃N was employed (entries 8–10). From the activity of several palladium precursors examined under the employed conditions, PdCl₂ combined with dppe [1,1'-bis(diphenylphosphino)ferrocene] exhibited similar catalytic activity to PdCl₂ combined with dppp (entries 3, 11–14). As a result, the best result in terms of product **3a** yield and complete conversion of **1a** was accomplished by the standard set of reaction conditions shown in entry 3 of Table 1.

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Table 1. Optimization of conditions for the reaction of **1a** with **2**^a

$$\text{1a} + \text{2} \xrightarrow[\text{(10 atm)}]{\text{cat. [Pd], CO}} \text{3a}$$

Entry	[2]/ [1a]	Pd catalyst	Base	Solvent	Time (h)	Yield (%)
1	1	PdCl ₂ /dppp	Et ₃ N	THF	15	30
2	2	PdCl ₂ /dppp	Et ₃ N	THF	3	55
3	3	PdCl ₂ /dppp	Et ₃ N	THF	3	62
4 ^b	3	PdCl ₂ /dppp	Et ₃ N	THF	3	50
5	5	PdCl ₂ /dppp	-	THF	15	54
6	3	PdCl ₂ /dppp	Et ₃ N	DMF	3	17
7	3	PdCl ₂ /dppp	Et ₃ N	Dioxane	3	57
8	3	PdCl ₂ /dppp	Et ₃ N	MeCN	15	38
9	3	PdCl ₂ /dppp	Na ₂ CO ₃	MeCN	15	22
10	3	PdCl ₂ /dppp	NaOAc	MeCN	15	32
11	3	PdCl ₂ (PPh ₃) ₂	Et ₃ N	THF	3	18
12	3	Pd(OAc) ₂ /PPh ₃	Et ₃ N	THF	3	2
13	3	PdCl ₂ (PhCN) ₂	Et ₃ N	THF	3	2
14	3	PdCl ₂ /dppf	Et ₃ N	THF	3	62

^aReaction conditions: **1a** (0.5 mmol), palladium catalyst (0.025 mmol), ligand (bidentate ligand: 0.03 mmol; PPh₃: 0.05 mmol), base (2 mmol), solvent (7 ml), CO (10 atm), 120 °C.

^bUnder CO (5 atm).

After the reaction conditions had been optimized, various β -bromo- α,β -unsaturated carboxylic acids **1** were subjected to the reaction with **2** in order to investigate the reaction scope, and several representative results are summarized in Table 2.^[14,15,31] From the carbonylative cyclization of six-membered β -bromo- α,β -unsaturated carboxylic acids **1b** and **1c** with **2**, the corresponding 1-(dimethylamino)-1*H*-pyrrole-2,5-diones **3b** and **3c** were also produced in similar yields irrespective of methyl and phenyl substituents on **1b** and **1c**. With β -bromo- α,β -unsaturated carboxylic acids (**1d–f**) having various ring sizes, the carbonylative cyclized products (**3d–f**) were produced in the range of 48–84% yields, and higher yield was observed with eight- and 12-membered β -bromo- α,β -unsaturated carboxylic acids **1e** and **1f**. However, not shown in Table 2, similar treatment of five-membered β -bromo- α,β -unsaturated carboxylic acid with **2** did not afford the corresponding product at all. To test for the effect of the position of bromide and carboxy group on β -bromo- α,β -unsaturated carboxylic acids **1g** and **1h** were employed. The carbonylative cyclization similarly took place with both **1g** and **1h** irrespective of their positions. However, lower reaction rate and yield were observed with acyclic β -bromo- α,β -unsaturated carboxylic acids (**1i** and **1j**).

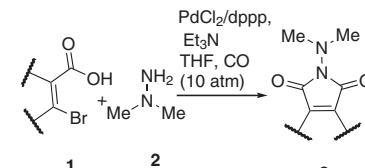
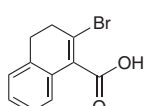
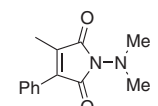
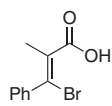
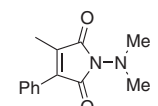
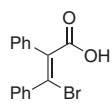
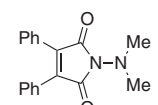
On the other hand, not shown in Table 2, similar treatment of **1a** with hydrazine hydrate (50–60%) did not afford an identifiable product at all. However, the reaction of **1a** with phenylhydrazine under the employed conditions afforded 4,5,6,7-tetrahydro-2-(phenylamino)-2*H*-isoindole-1,3-dione (**3j**) in 45% yield.

Table 2. Palladium-catalyzed synthesis of 1-(dimethylamino)-1*H*-pyrrole-2,5-diones^a

1	3	Isolated yield (%)
		62
		56
		40
		48
		80
		84
		54

(Continues)

Table 2. (Continued)

		
1	3	Isolated yield (%)
 1h	 3g	41
 1i	 3h	10
 1j	 3i	33
^a Reaction conditions: 1 (0.5 mmol), 2 (1.5 mmol), PdCl ₂ (0.025 mmol), dppp (0.03 mmol), Et ₃ N (2 mmol), THF (7 ml), CO (10 atm), 120 °C, 3 h.		

Conclusion

In summary, it has been shown that β -bromo- α,β -unsaturated carboxylic acids, which are readily prepared from α -methylene-containing ketones under the bromination conditions of Vilsmeier–Haak reaction and subsequent oxidation, undergo carbonylative cyclization with 2,2-dimethylhydrazine in the presence of a palladium catalyst to give 1-(dimethylamino)-1H-pyrrole-2,5-diones. We believe that the products prepared by the present reaction will be used as precursors for various valuable heterocyclic compounds. Further study of synthetic applications to heterocycles starting from ketones is in progress.

Experimental

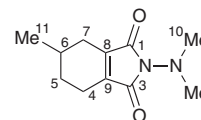
¹H and ¹³C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Stanford Research Inc. MPA100 automated melting point apparatus. High-resolution mass spectrometry (HRMS) was performed with a Jeol JMS-700 spectrometer at the Korea Basic Science Center, Daegu, Korea. The isolation of pure products was carried out via thin-layer (silica gel 60 GF₂₅₄, Merck) or column (silica gel 60, 70–230 mesh, Merck) chromatography.

The starting β -bromo- α,β -unsaturated carboxylic acids were prepared via two steps from the corresponding ketones according to literature procedures.^[14,15,31] Commercially available organic and inorganic compounds were used without further purification.

General Procedure for Palladium-Catalyzed Carbonylative Cyclization of β -Bromo- α,β -Unsaturated Carboxylic Acids with *N,N*-Dimethylhydrazine Leading to 1-(Dimethylamino)-1H-Pyrrole-2,5-Diones

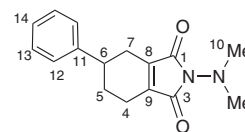
To a 50 ml stainless steel autoclave were added β -bromo- α,β -unsaturated carboxylic acid **1** (0.5 mmol), *N,N*-dimethylhydrazine (**2**) (0.090 g, 1.5 mmol), PdCl₂ (0.004 g, 0.025 mmol), dppp (0.012 g, 0.03 mmol), Et₃N (0.202 g, 2 mmol) and THF (7 ml). After the system was flushed and then pressurized with CO to 10 atm, the reaction mixture was allowed to react at 120 °C for 3 h. The reaction mixture was filtered through a short silica gel column (ethyl acetate) to eliminate inorganic salts. Removal of the solvent left a crude mixture, which was separated by thin-layer chromatography (silica gel, ethyl acetate–hexane mixture) to give 1-(dimethylamino)-1H-pyrrole-2,5-diones **3**. Except for known **3a**^[30] and **3i**,^[32] all new products prepared by the above procedure were characterized spectroscopically as shown below.

2-(Dimethylamino)-4,5,6,7-tetrahydro-6-methyl-2H-isoindole-1,3-dione (**3b**)



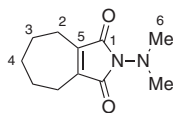
Oil. ¹H NMR (400 MHz, CDCl₃) δ 1.08 (d, *J*_{HH} = 6.3 Hz, 3H, CHCH₃), 1.28–1.38 (m, 1H, CH₂/2), 1.74–1.92 (m, 3H, CH and 2CH₂/2), 2.21–2.31 (m, 1H, CH₂/2), 2.41–2.50 (m, 2H, CH₂), 2.91 (s, 6H, 2CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 19.88 (C11), 21.27 (C4), 27.94 (C6), 28.04 (C5), 29.59 (C7), 45.09 (C10), 139.81 (C9), 139.89 (C8), 169.70 (C1), assignments to C5–C7 are interchangeable, assignments to C8 and C9 are interchangeable. Anal. Calcd for C₁₁H₁₆N₂O₂: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.24; H, 7.70; N, 13.33.

2-(Dimethylamino)-4,5,6,7-tetrahydro-6-phenyl-2H-isoindole-1,3-dione (**3c**)



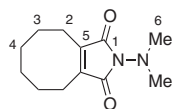
Oil. ¹H NMR (400 MHz, CDCl₃) δ 1.77–1.88 (m, 1H, CH₂/2), 2.13–2.17 (m, 1H, CH₂/2), 2.33–2.47 (m, 2H, CH₂), 2.54–2.60 (m, 1H, CH₂/2), 2.69–2.76 (m, 1H, CH₂/2), 2.85–2.98 (m, 1H, CH), 2.93 (s, 6H, 2CH₃), 7.21–7.28 (m, 3H, phenyl 3CH), 7.32–7.36 (m, 2H, phenyl 2CH). ¹³C NMR (100 MHz, CDCl₃) δ 20.76 (C4), 27.62 (C5), 29.03 (C7), 39.38 (C6), 45.12 (C10), 126.85 (C12), 126.92 (C14), 128.86 (C13), 139.81 (C11), 139.82 (C9), 144.54 (C8), 169.43 (C1 and C3), assignments to C12–C14 are interchangeable, assignments to C8, C9 and C11 are interchangeable. Anal. Calcd for C₁₆H₁₈N₂O₂: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.95; H, 6.70; N, 10.38.

2-(Dimethylamino)-4,5,6,7-tetrahydrocyclohepta[c]pyrrole-1,3(2H,4H)-dione (**3d**)



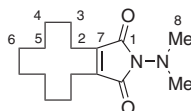
Oil. ^1H NMR (400 MHz, CDCl_3) δ 1.64–1.70 (m, 4H, 2CH_2), 1.77–1.83 (m, 2H, CH_2), 2.49–2.52 (m, 4H, allylic 2CH_2), 2.91 (s, 6H, 2CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 24.67 (C3), 26.60 (C2), 30.26 (C4), 44.99 (C6), 140.93 (C5), 170.48 (C1), assignments to C2 and C3 are interchangeable. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.37; H, 7.70; N, 13.48.

2-(Dimethylamino)-4,5,6,7,8,9-hexahydro-2H-cycloocta[c]pyrrole-1,3-dione (**3e**)



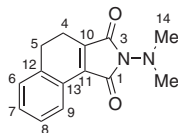
Oil. ^1H NMR (400 MHz, CDCl_3) δ 1.53–1.59 [m, 4H, $-(\text{CH}_2)_2-$], 1.74–1.80 (m, 4H, 2CH_2), 2.54–2.57 (m, 4H, allylic 2CH_2), 2.91 (s, 6H, 2CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 22.15 (C4), 25.72 (C3), 26.52 (C2), 45.11 (C6), 139.60 (C5), 170.64 (C1). Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2$: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.72; H, 8.10; N, 12.50.

2-(Dimethylamino)-4,5,6,7,8,9,10,11,12,13-decahydro-2H-cyclododeca[c]pyrrole-1,3-dione (**3f**)



Oil. ^1H NMR (400 MHz, CDCl_3) δ 1.24–1.44 [m, 12H, $-(\text{CH}_2)_6-$], 1.69–1.75 (m, 4H, 2CH_2), 2.38–2.42 (m, 4H, allylic 2CH_2), 2.91 (s, 6H, 2CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 21.43 (C6), 22.28 (C5), 24.51 (C4), 25.31 (C3), 26.11 (C2), 45.12 (C8), 140.07 (C7), 170.57 (C1), assignments to C5 and C6 are interchangeable. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{N}_2\text{O}_2$: C, 69.03; H, 9.41; N, 10.06. Found: C, 68.92; H, 9.20; N, 10.11.

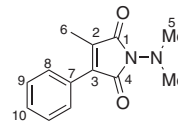
2-(Dimethylamino)-4,5-dihydro-2H-benzo[e]isoindole-1,3-dione (**3g**)



Solid. m.p. 169–170 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.66 (t, $J_{\text{HH}} = 8.5$ Hz, 2H, benzylic CH_2), 2.98 (s, 6H, 2CH_3), 3.00 (t, $J_{\text{HH}} = 8.5$ Hz, 2H, allylic CH_2), 7.21–7.23 (m, 1H, CH), 7.25–7.34 (m, 2H, 2CH), 8.09–8.11 (m, 1H, CH). ^{13}C NMR (100 MHz, CDCl_3) δ 18.05 (C5), 27.27 (C4), 45.16 (C14), 126.18 (C8), 126.68 (C13), 127.43 (C9), 128.58 (C6), 130.71 (C7), 134.33 (C12), 136.10 (C10), 137.03 (C11), 168.60 (C1), 169.25 (C3), assignments to C1 and C3 are interchangeable, assignments to C6–C8 are interchangeable. HRMS (EI). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$ (M^+): 242.1055. Found:

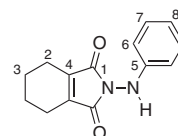
242.1058. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.32; H, 5.69; N, 11.47.

1-(Dimethylamino)-3-methyl-4-phenyl-1H-pyrrole-2,5-dione (**3h**)



Oil. ^1H NMR (400 MHz, CDCl_3) δ 2.19 (s, 3H, CCH_3), 2.97 (s, 6H, 2CH_3), 7.41–7.50 (m, 3H, phenyl 3CH), 7.55–7.58 (m, 2H, phenyl 2CH). ^{13}C NMR (100 MHz, CDCl_3) δ 10.15 (C6), 45.14 (C5), 128.80 (C8), 128.92 (C7), 129.74 (C9), 129.89 (C10), 135.19 (C2), 135.82 (C3), 169.64 (C4), 170.53 (C1), assignments to C1 and C4 are interchangeable, assignments to C2 and C3 are interchangeable. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.60; H, 6.09; N, 12.11.

4,5,6,7-Tetrahydro-2-(phenylamino)-2H-isoindole-1,3-dione (**3j**)



Semi-solid. ^1H NMR (400 MHz, CDCl_3) δ 1.77–1.80 [m, 4H, $-(\text{CH}_2)_2-$], 2.35–2.38 (m, 4H, 2CH_2), 6.10 (s, 1H, NH), 6.73–6.75 (m, 2H, phenyl 2CH), 6.89–6.93 (m, 1H, phenyl CH), 7.18–7.22 (m, 2H, phenyl 2CH). ^{13}C NMR (100 MHz, CDCl_3) δ 20.23 (C3), 21.30 (C2), 113.85 (C6), 122.05 (C8), 129.38 (C7), 140.61 (C4), 146.24 (C5), 169.23 (C1), assignments to C4 and C5 are interchangeable. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.50; H, 5.80; N, 11.51.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0007563) and Kyungpook National University Research Fund, 2013.

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