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Palladium-catalyzed Carbonylative Cyclization of 2-Bromocyclohex-1-enecarbaldehydes with Aliphatic Primary Amines Leading to 3-Aminohydroisoindol-1-ones

Yeon Kyu Bae, Chan Sik Cho,* and Nam Sik Yoon†

*Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, Korea. *E-mail: cscho@knu.ac.kr*
†Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Korea
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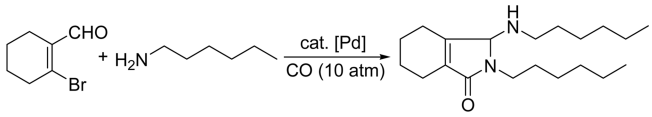
Palladium-catalyzed carbonylation of organic halides (or triflates) followed by intramolecular cyclization (carbonylative cyclization) has been widely explored and used as a promising synthetic tool for the construction of the structural core of many pharmacologically and biologically active lactones and lactams.[1] During the course of our ongoing studies on palladium-catalyzed cyclization reactions using β-bromo-α,β-unsaturated aldehydes and their derivatives,[2] which are readily prepared from the corresponding ketones by bromination conditions of Vilsmeier-Haak reaction[3,4] and subsequent transformation and used as a building block for the synthesis of versatile cyclic compounds,[5,6] we also recently reported on the synthesis of several heterocycles *via* such an intrinsic carbonylative cyclization.[7] Among them, in connection with this report, 2-bromocyclohex-1-enecarbaldehydes were found to be carbonylatively cyclized with primary aromatic amines under carbon monoxide pressure in the presence of a palladium catalyst to afford hydroisoindol-1-ones which have no substituents at position 3 *via* an intramolecular acylpalladation to carbon-nitrogen double bond followed by protonation (Scheme 1, route a).[7c,8,9] This protocol led us to extend to the reaction with more nucleophilic aliphatic primary amines. This report describes a palladium-catalyzed synthesis of 3-aminohydroisoindol-1-ones from 2-bromocyclohex-1-enecarbaldehydes and aliphatic primary amines *via* such an intrinsic carbonylative cyclization followed by final substitution with aliphatic primary amines (Scheme 1, route b).[2b,2d,10] It is known that basic framework of 3-aminohydroisoindol-1-ones, 1,5-dihydro-2*H*-pyrrol-2-ones are widely used as herbicide components and building blocks for syntheses of complex natural products.[11]

The results of several attempted carbonylative cyclizations of 2-bromocyclohex-1-enecarbaldehyde (**1a**) with hexylamine (**2a**) under various conditions are listed in Table 1. Treatment of **1a** with four equivalents of **2a** in DMF in the presence of $Pd(OAc)_2$ (4 mol %) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) (6 mol %) along with Et_3N at 100 °C for 20 h afforded 2-hexyl-3-(hexylamino)-2,3,4,5,6,7-hexahydroisoindol-1-one (**3a**) in 44% isolated yield (run 1).

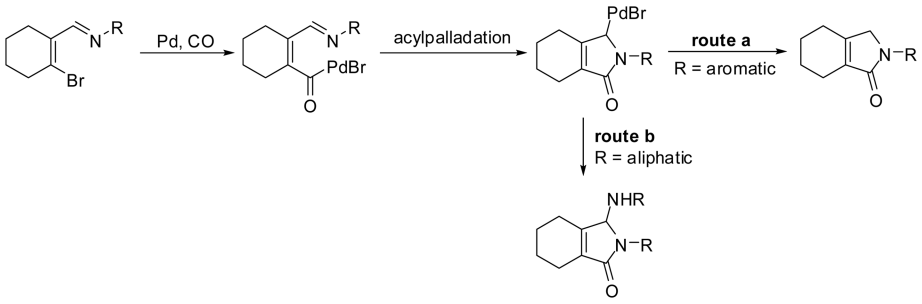
Table 1. Optimization of conditions for the reaction of **1a** with **2a**[a]



1a **2a** **3a**

Run	[**2a**]/[**1a**]	Pd catalyst	Base	Solvent	Yield (%)
1	4	$Pd(OAc)_2$/dppf	Et_3N[b]	DMF	44
2	4	$Pd(OAc)_2$/dppf	Et_3N[b]	dioxane	7
3	4	$Pd(OAc)_2$/dppf	Et_3N[b]	toluene	7
4	4	$Pd(OAc)_2$/dppf	Et_3N[b]	MeCN	24
5	4	$Pd(OAc)_2$/dppf	K_3PO_4	DMF	16
6	4	$Pd(OAc)_2$/dppf	K_2CO_3	DMF	57
7	2	$Pd(OAc)_2$/dppf	K_2CO_3	DMF	34
8	4	$Pd(OAc)_2$/dppp	K_2CO_3	DMF	60
9	4	$Pd(OAc)_2$/PPh_3	K_2CO_3	DMF	35
10	4	$PdCl_2(PPh_3)_2$	K_2CO_3	DMF	16
11	4	$PdCl_2$/dppp	K_2CO_3	DMF	80

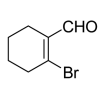
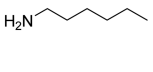
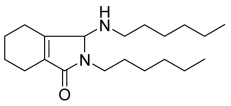
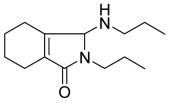
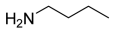
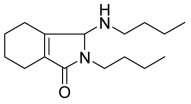
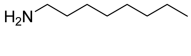
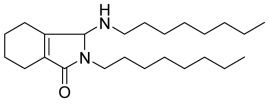
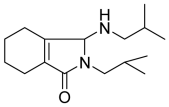
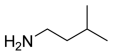
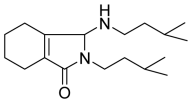
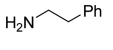
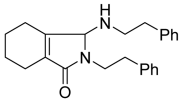
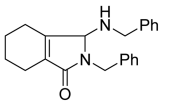
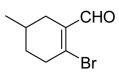
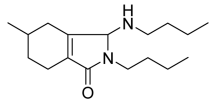
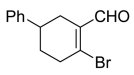
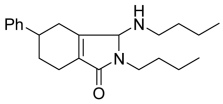
[a]Reaction conditions: **1a** (0.5 mmol), palladium catalyst (0.02 mmol), ligand (bidentate ligand: 0.03 mmol; monodetate ligand: 0.04 mmol), base (2 mmol), solvent (10 mL), CO (10 atm), 100 °C, for 20 h. [b]4 mmol.



Scheme 1

Other solvents such as dioxane, toluene and MeCN under the conditions of $Pd(OAc)_2$/dppf/Et_3N were not effective for the present carbonylative cyclization (runs 1-4). Among bases examined, K_2CO_3 revealed to be the base of choice under the conditions of $Pd(OAc)_2$/dppf/DMF (runs 1, 5, 6). Lower molar ratio of **2a** to **1a** resulted in lower yield of **3a** (run 7). From the activity of several palladium precursors examined under the employed conditions, catalytic systems of $Pd(OAc)_2$ or $PdCl_2$ combined with phosphorus chelating ligands generally gave higher yield of **3a** (runs 6, 8-11). The catalytic system of $Pd(OAc)_2$ combined with 1,3-bis(diphenylphosphino)propane exhibited nearly the same catalytic activity as that of $Pd(OAc)_2$ combined with dppf (run 8). Palladium precursors such as $Pd(OAc)_2$ combined with PPh_3 and $PdCl_2(PPh_3)_2$ were revealed to be ineffective (runs 9 and 10). As a result, the best result was accomplished under the catalytic system of $PdCl_2$ combined with dppp shown in run 11 of Table 1.

Table 2. Palladium-catalyzed carbonylative cyclization of 2-bromocyclohex-1-enecarbaldehydes **1** with aliphatic primary amines **2** leading to 3-aminohydroisoindol-1-ones **3**[a]

1	2	3	Yield (%)
 **1a**	 **2a**	 **3a**	80
	 **2b**	 **3b**	74
	 **2c**	 **3c**	87
	 **2d**	 **3d**	71
	 **2e**	 **3e**	79
	 **2f**	 **3f**	58
	 **2g**	 **3g**	57
	 **2h**	 **3h**	45
 **1b**	**2c**	 **3i**	70
 **1c**	**2c**	 **3j**	45

[a]Reaction conditions: **1** (0.5 mmol), **2** (2 mmol), $PdCl_2$ (0.02 mmol), dppp (0.03 mmol), K_2CO_3 (2 mmol), DMF (10 mL), CO (10 atm), 100 °C, 20 h.

After the reaction conditions had been established, several 2-bromocyclohex-1-enecarbaldehydes **1** were subjected to reaction with various aliphatic primary amines **2** in order to investigate the reaction scope and several representative results are summarized in Table 2. 2-Bromocyclohex-1-enecarbaldehyde (**1a**) reacted with an array of aliphatic primary amines (**2a-d**) having straight alkyl chains and the corresponding 3-aminohydroisoindol-1-ones (**3a-d**) were obtained in a range of 71-87% isolated yields.[12,13] The product yield was not significantly affected by the alkyl chain length on **2a-d**. In the reaction with aliphatic primary amines (**2e** and **2f**) having branched alkyl chains, similar reaction rate and yield were observed with isobuylamine (**2e**), whereas lower yield of 3-aminohydroisoindol-1-one **3f** was obtained with isoamylamine (**2f**). The reaction of **1a** with phenethylamine (**2g**) and benzylamine (**2h**) having phenyl substituent also proceeds to give the corresponding 3-aminehydroisoindol-1-ones (**3g** and **3h**), and the product yield was lower than that when aliphatic primary amines (**2a-d**) were used. 2-Bromo-5-methylcyclohex-1-enecarbaldehyde (**1b**) and 2-bromo-5-phenylcyclohex-1-enecarbaldehyde (**1c**) also react with butylamine (**2c**) to afford the corresponding 3-aminohydroisoindol-1-ones **3i** and **3j** as a diastereoisomeric mixture in 70% and 45% yields, respectively.

In summary, it has been shown that 2-bromocyclohex-1-enecarbaldehydes, which are readily prepared from α-methylene containing cyclohexanones under the bromination conditions of Vilsmeier-Haak reaction, undergo carbonylative cyclization with aliphatic primary amines in the presence of a palladium catalyst and a bidentate phosphorus ligand to give 3-aminohydroisoindol-1-ones. The present reaction provides a promising route for the synthesis of valuable heterocycles from readily available starting ketones. Further study of synthetic applications to heterocycles using these ketones is currently under investigation.

Experimental Section

^1H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using TMS as an internal standard. Melting points were determined on a Stanford Research Inc. MPA100 automated melting point apparatus. HRMS was performed at the Korea Basic Science Institute (Daegu). The isolation of pure products was carried out *via* thin layer (silica gel 60 GF_{254}, Merck) chromato-

graphy. The starting 2-bromocyclohex-1-enecarbaldehydes **1** were synthesized from the corresponding cyclohexanones according to literature procedures.[3,4] Commercially available organic and inorganic compounds were used without further purification.

Typical Experimental Procedure. To a 50 mL stainless steel autoclave were added 2-bromocyclohex-1-enecarbaldehyde (**1a**) (0.095 g, 0.5 mmol), hexylamine (**2a**) (0.202 g, 2 mmol), $PdCl_2$ (0.004 g, 0.02 mmol), dppp (0.012 g, 0.03 mmol), K_2CO_3 (0.276 g, 2 mmol) and dry DMF (10 mL). After the system was flushed and then pressurized with carbon monoxide to 10 atm, the reaction mixture was allowed to react at 100 °C for 20 h. The reaction mixture was filtered through a short silica gel column (ethyl acetate-hexane mixture) to eliminate catalyst residue. Removal of the solvent left a crude mixture, which was separated by thin layer chromatography (silica gel, ethyl acetate- hexane = 1/10) to give 2-hexyl-3-(hexylamino)-2,3,4,5,6,7-hexahydroisoindol-1-one (**3a**) (0.128 g, 80%). All new products prepared by the above procedure were characterized spectroscopically as shown below.

2-Hexyl-3-(hexylamino)-2,3,4,5,6,7-hexahydroisoindol-1-one (3a). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.89 (m, 6H), 1.26-1.51 (m, 16H), 1.68-1.76 (m, 5H), 2.07-2.31 (m, 6H), 2.91-2.98 (m, 1H), 3.62-3.70 (m, 1H), 4.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.05 (x2), 20.19, 22.06, 22.24, 22.59, 22.61, 22.97, 26.79, 27.02, 29.02, 30.35, 31.62, 31.71, 38.74, 40.69, 74.10, 133.55, 151.24, 170.71; HRMS (EI) Anal. Calcd for $C_{20}H_{36}N_2O$ (M^+): 320.2828. Found: 320.2828.

2,3,4,5,6,7-Hexahydro-2-propyl-3-(propylamino)isoindol-1-one (3b). Solid; mp 49-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88-0.93 (m, 6H), 1.36-1.47 (m, 2H), 1.50-1.61 (m, 2H), 1.67-1.77 (m, 5H), 2.05-2.29 (m, 6H), 2.90-2.97 (m, 1H), 3.60-3.67 (m, 1H), 4.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.72, 12.06, 20.36, 22.22, 22.39, 22.41, 23.12, 23.67, 40.50, 42.72, 74.20, 133.71, 151.42, 170.96; HRMS (EI) Anal. Calcd for $C_{14}H_{24}N_2O$ (M^+): 236.1889. Found: 236.1890.

2-Butyl-3-(butylamino)-2,3,4,5,6,7-hexahydroisoindol-1-one (3c). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H), 1.26-1.43 (m, 6H), 1.47-1.55 (m, 2H), 1.67-1.77 (m, 5H), 2.05-2.35 (m, 6H), 2.17-2.32 (m, 5H), 2.92-2.98 (m, 1H), 3.65-3.72 (m, 1H), 4.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.01, 14.12, 20.33, 20.44, 20.63, 22.21, 22.39, 23.11, 31.30, 32.66, 38.51, 40.49, 74.18, 133.69, 151.37, 170.88; HRMS (FAB) Anal. Calcd for $C_{16}H_{29}N_2O$ ([M + H]$^+$): 265.2280. Found: 265.2278.

2,3,4,5,6,7-Hexahydro-2-octyl-3-(octylamino)isoindol-1-one (3d). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.89 (m, 6H), 1.26-1.40 (m, 22H), 1.48-1.56 (m, 2H), 1.68-1.76 (m, 5H), 2.06-2.34 (m, 6H), 2.91-2.98 (m, 1H), 3.62-3.70 (m, 1H), 4.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.25 (x2), 20.33, 22.20, 22.38, 22.80 (x2), 23.10, 27.26, 27.49, 29.20, 29.38, 29.40, 29.53, 29.61, 30.51, 31.98 (x2), 38.86, 40.77, 74.21, 133.69, 151.34, 170.84; HRMS (EI) Anal. Calcd for $C_{24}H_{44}N_2O$ (M^+): 376.3454. Found: 376.3456.

2,3,4,5,6,7-Hexahydro-2-isobutyl-3-(isobutylamino)isoindol-1-one (3e). Solid; mp 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, J = 6.5 Hz, 3H), 0.88 (d, J = 6.5 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 1.54-1.64 (m, 1H), 1.69-1.80 (m, 5H), 1.84-1.94 (m, 2H), 2.07-2.29 (m, 5H), 2.72-2.77 (m, 1H), 3.48-3.54 (m, 1H), 4.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.13, 20.19, 20.54, 20.66, 20.76, 22.06, 22.22, 22.94, 28.21, 28.84, 45.94, 48.59, 74.42, 133.44, 151.23, 170.98; HRMS (EI) Anal. Calcd for $C_{16}H_{28}N_2O$ (M^+): 264.2202. Found: 264.2202.

2,3,4,5,6,7-Hexahydro-2-isopentyl-3-(isopentylamino)-isoindol-1-one (3f). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, J = 6.6 Hz, 6H), 0.93 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H), 1.23-1.34 (m, 2H), 1.35-1.47 (m, 2H), 1.51-1.80 (m, 7H), 2.09-2.35 (m, 6H), 2.93-3.00 (m, 1H), 3.68-3.75 (m, 1H), 4.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.35, 22.23, 22.41, 22.58, 22.78, 22.82, 22.89, 23.15, 26.10, 26.19, 37.14, 38.01, 38.91, 39.69, 74.15, 133.75, 151.38, 170.82; HRMS (FAB) Anal. Calcd for $C_{18}H_{33}N_2O$ ([M + H]$^+$): 293.2593. Found: 293.2596.

2,3,4,5,6,7-Hexahydro-2-phenethyl-3-(phenethylamino)-isoindol-1-one (3g). Solid; mp 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63-1.74 (m, 5H), 1.99-1.21 (m, 4H), 2.31-2.37 (m, 1H), 2.43-2.49 (m, 1H), 2.59-2.66 (m, 1H), 2.69-2.78 (m, 3H), 2.83-2.94 (m, 1H), 3.83-3.90 (m, 1H), 4.33 (s, 1H), 7.05-7.07 (m, 2H), 7.14-7.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.28, 22.12, 22.30, 22.97, 35.46, 36.36, 40.13, 41.87, 74.37, 126.53, 126.63, 128.68, 128.74, 128.79, 128.90, 133.70, 139.52, 139.79, 151.57, 170.83; HRMS (EI) Anal. Calcd for $C_{24}H_{28}N_2O$ (M^+): 360.2202. Found: 360.2203.

2-Benzyl-3-(benzylamino)-2,3,4,5,6,7-hexahydroisoindol-1-one (3h). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.75 (m, 4H), 1.96 (s, 1H), 2.08-2.13 (m, 1H), 2.20-2.27 (m, 3H), 3.31 (d, J = 13.0 Hz, 1H), 3.39 (d, J = 13.0 Hz, 1H), 4.19 (d, J = 15.0 Hz, 1H), 4.65 (s, 1H), 4.96 (d, J = 15.0 Hz, 1H), 7.18-7.27 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.65, 22.34, 22.48, 23.44, 43.50, 45.78, 74.28, 127.55, 127.78, 128.55 (x2), 128.79, 129.10, 133.98, 138.42, 140.16, 152.27, 171.21; HRMS (EI) Anal. Calcd for $C_{22}H_{24}N_2O$ (M^+): 332.1889. Found: 332.1891.

2-Butyl-3-(butylamino)-2,3,4,5,6,7-hexahydro-5-methyl-isoindol-1-one (3i). Oil; diastereoisomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87-0.95 (m, 6H), 1.05 (t, J = 6.8 Hz, 3H), 1.24-1.43 (m, 7H), 1.47-1.55 (m, 2H), 1.69-1.90 (m, 4H), 2.05-2.22 (m, 2H), 2.25-2.38 (m, 3H), 2.91-2.99 (m, 1H), 3.64-3.72 (m, 1H), 4.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.45 (N*C*H$_2$), 38.54 (N*C*H$_2$), 40.40 (NH*C*H$_2$), 40.45 (NH*C*H$_2$), 73.78 (N*C*HN), 74.16 (N*C*HN), 133.30 (C=*C*CO), 133.41 (C=*C*CO), 151.02 (*C*=CCO), 151.36 (*C*=CCO), 170.68 (*C*=O), 170.70 (*C*=O); HRMS (EI) Anal. Calcd for $C_{17}H_{30}N_2O$ (M^+): 278.2358. Found: 278.2357.

2-Butyl-3-(butylamino)-2,3,4,5,6,7-hexahydro-5-phenyl-isoindol-1-one (3j). Oil; diastereoisomeric mixture; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H), 1.25-1.42 (m, 6H), 1.49-1.56 (m, 2H), 1.64-1.83 (m, 2H), 2.05-2.37 (m, 5H), 2.44-2.63 (m, 2H), 2.79-3.02

(m, 2H), 3.67-3.75 (m, 1H), 4.73 (s, 1/2H), 4.75 (s, 1/2H), 7.22-7.26 (m, 3H), 7.32-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.75 (NCHN), 74.36 (NCHN), 133.49 (C=CCO), 133.54 (C=CCO), 145.91 (phenylCCH), 145.97 (phenyl-CCH), 151.07 (C=CCO), 151.34 (C=CCO), 170.42 (C=O), 170.45 (C=O); HRMS (EI) Anal. Calcd for $C_{22}H_{32}N_2O$ (M^+): 340.2515. Found: 340.2513.

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12. Treatment of **1a** with ethylamine (70 wt % in H_2O) under the employed conditions did not afford the corresponding 3-amino-hydroisoindol-1-one at all.
13. Similar treatment of **1a** with secondary amine, dibutylamine did not proceed toward the carbonylative cyclization under the same conditions.